ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

FUNCTIONAL HIGH PERFORMANCE POLYBENZOXAZINES AND THEIR PROPERTIES

Ph.D. THESIS

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

YÜKSEK PERFORMANSLI FONKSİYONEL POLİBENZOKSAZİNLER VE ÖZELLİKLERİ

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To my parent and my wife

FOREWORD

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(M.Sc. Chemist)

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ABBREVIATIONS

ATRP	**:** Atom Transfer Radical Polymerization
$CDCl_3$	**:** Deuterated Chloroform
CH_2Cl_2	**:** Dichloromethane
Conv	**:** Conversion
CuAAC	**:** Copper Catalyzed Azide-Alkyne Cycloaddition
DMF	**:** *N, N*-Dimehthylformamide
DMSO	**:** Dimethyl Sulphoxide
FT-IR	**:** Fourier Transform Infrared Spectrophotometer
GPC	**:** Gel Permeation Chromatography
^{1}H NMR	**:** Hydrogen Nuclear Magnetic Resonance Spectroscopy
M_n	**:** Number Avarage Molecular Weight
PDI	**:** Polydispersity
PEO	**:** Poly(ethylene oxide)
ROP	**:** Ring-opening Polymerization
THF	**:** Tetrahydrofuran
UV	**:** Ultraviolet
PPO-Benz	**:** Poly(propylene oxide) Benzoxazine
PPO	**:** Poly(propylene oxide) Bisamine
Carb-Benz	**:** Carboxlic Acid Containing Benzoxazine
BA-ala	**:** Allyl Functional Benzoxazine
TGA	**:** Thermogravimetric Analysis
DSC	**:** Differential Scanning Calorimetry
SEM	**:** Scanning Electron Microscope
PB	**:** Polybutadiene
BPh-ptol	**:** Benzophenone Benzoxazine
Van-a	**:** Vanillin Benzoxazine
DMA	**:** Dynamic Mechanical Analysis
S_8	**:** Cyclooctasulfur
TEMPO	**:** 2,2,6,6-Tetramethyl-1-piperidinyloxy
ABS	**:** Acrylonitrile-butadiene-styrene
4-HBPh	**:** 4-Hydroxybenzophenone

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FUNCTIONAL HIGH PERFORMANCE POLYBENZOXAZINES AND THEIR PROPERTIES

SUMMARY

Phenolic resins are leading the polymer market due to their widespread applications such as adhesives, structural applications materials in aerospace, printed circuit boards, conductive polymer elements, and encapsulation materials for electronic applications. Phenolic resins, acrylates, bismaleimides, polyesters, epoxy resins and isocyanate polymers are the best known members of the thermosets. High processing temperatures and void formation during curing are the main challenges must be overcome regarding application of these materials. Lately, benzoxazine based phenolic resins has been developed and attracted significant attention as a novel type of phenolic resin. Polybenzoxazines have various outstanding properties, including good thermal stability, high glass transition temperature, high char yield, no need of catalysts for curing, near-zero volume changes during curing, low moisture absorption and no volatile release. Recently, owing to the design flexibility of benzoxazine and related polymeric benzoxazine precursors, various smart materials were synthesized by innovative strategies including self-healing materials, electrochemically activated smart coatings, smart sorbents for heavy metals, hydrophobic surface applications and porous polybenzoxazine resins. Taking account of the unique advantages of these strategies and attractive characteristics of polybenzoxazines, in this thesis, we focused on the combination of various functional groups with benzoxazine precursors and then investigated the resulted products properties.

In the first part of the thesis, a self-healing strategy for poly(propylene oxide)s bearing benzoxazine units (PPO-Benz) through supramolecular attractions is described. Poly(propylene oxide) bisamine (PPO) with a molecular wieght of 2000 Da were reacted with formaldehyde and bisphenol A to yield desired PPO-Benz with 12360 Da. The cross-linked polymer films were then prepared by solvent casting of suitable compositions of PPO-Benz and carboxlic acid containing benzoxazine monomer (Carb-Benz) in chloroform followed by thermal ring opening reaction of benzoxazine groups at 200 °C. Thermal curing and thermal stability of the film and final products were investigated. It was demonstrated that the self-healing capacity of the films were improved by employing Carb-Benz in the formulation.

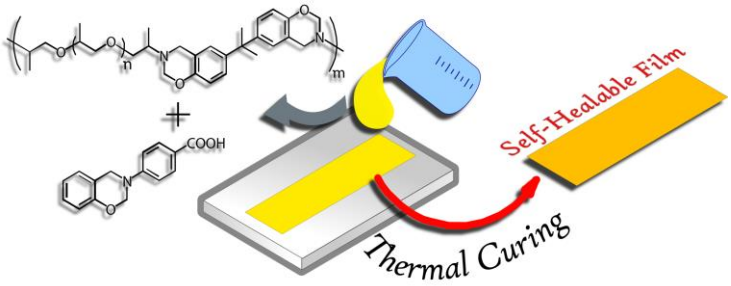


Figure 1 : Self-healable film preparation from carboxylic acid containing benzoxazine monomer and PPO-Benz.

In the second part of the thesis, a novel strategy to obtain sulfur rich polybenzoxazine copolymers by reacting allyl functional benzoxazine (BA-ala) and elemental sulfur was described. Simultaneous inverse vulcanization and ring-opening reactions of benzoxazine generated soluble copolymers in specific feed ratios. Parameters such as monomer structure and feed ratios on the polymerization were studied. The thermal stability of the copolymers was investigated and compared to that of polybenzoxazines derived from neat BA-ala by using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The surface properties of the materials as examined by scanning electron microscope (SEM) confirmed that elemental sulfur and benzoxazine copolymers can be produced without a phase separation at micrometer level. Moreover, a sponge like insoluble macroporous polybenzoxazine networks was obtained at the 20%-wt feed ratio of sulfur.

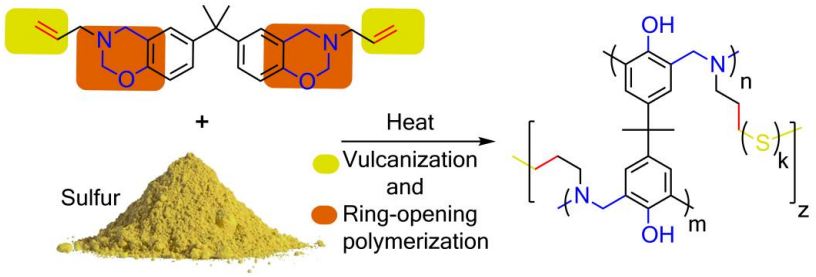


Figure 2 : A novel strategy to obtain sulfur rich polybenzoxazine copolymers by reacting allyl functional benzoxazine (BA-ala) and elemental sulfur.

Finally, side-chain benzoxazine functional polybutadienes was synthesized by photoinduced hydrogen abstraction process. First, photosensitive benzoxazine compounds possessing both chromophoric carbonyl and hydrogen donating sites in the structure were synthesized using vanillin or 4-hydroxybenzophenone in the conventional benzoxazine synthesis. Irradiation of neat polybutadiene (PB) in the presence of the corresponding benzoxazines, namely benzophenone benzoxazine (BPh-ptol) and vanillin benzoxazine (Van-a) under 300–350 nm light gave PBs with approximately 4-5 benzoxazine units per chain. Successful modification was confirmed by the spectral and thermal investigations. It is shown that benzoxazine modified PBs undergo thermally activated curing in the absence of any catalyst forming polybutadiene thermoset with high char yield.

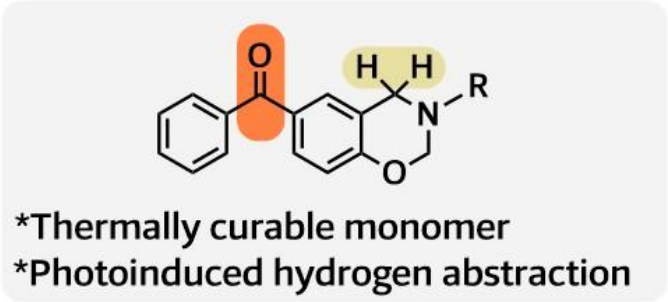


Figure 3 : Photoactive benzoxazines having both chromophoric carbonyl and hydrogen donating sites were synthesized using vanillin or 4-hydroxybenzophenone by conventional benzoxazine synthesis methodology.

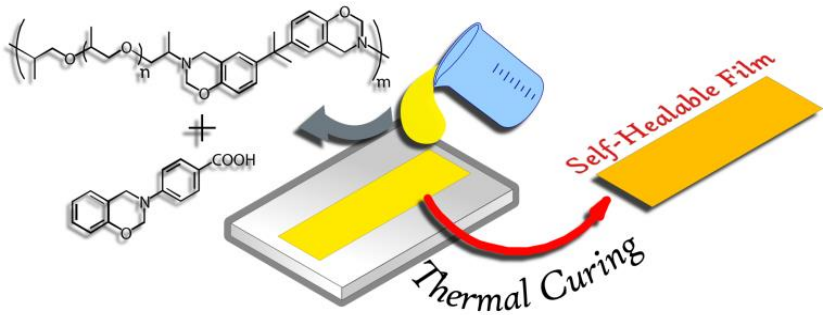
YÜKSEK PERFORMANSLI FONKSİYONEL POLİBENZOKSAZİNLER VE ÖZELLİKLERİ

ÖZET

Fenolik reçineler, yaygın uygulamaları sebebi ile yapıştırıcı sanayii'nde, havacılık yapı uygulamalarında, baskı devre kartlarında, iletken polimer yapılarda, malzeme kapsülleri ve elektronik olmak üzere çok çeşitli alanlarda kullanılmaktadır. Fenolik reçineler, akrilatlar, bismaleimidler, poliesterler, epoksi reçineler ve izosiyanat polimerler termosetlerin en iyi bilinen üyeleridir. Yüksek işlem sıcaklıkları ve kürleme sırasında gözenek oluşumu, bu malzemelerin aşılması gereken başlıca zorluklarıdır. Son zamanlarda, benzoksazin bazlı fenolik reçineler geliştirilmiş ve fenolik reçinelerin yeni bir türü olarak önemli derecede dikkat çekmiştir. Polibenzoksazinler; iyi bir ısıl kararlılık, yüksek camsı geçiş sıcaklığı, yüksek yanma ürünü, kürleme için katalizöre gerek olmaması, kürleme sırasında hacmi değişmemesi, düşük nem absorpsiyonu ve herhangi bir uçucu açığa çıkarmaması gibi üstün özelliklere sahiptir.

Son zamanlarda, benzoksazin monomerlerinin ve polimerik benzoksazin öncüllerinin tasarım esnekliği sayesinde, yenilikçi yaklaşımlar kullanılarak, kendi kendine iyileşebilen, elektrokimyasal olarak aktif hale gelebilen akıllı kaplamalar, ağır metaller için akıllı sorbentler, hidrofobik yüzeyler ve gözenekli polibenzoksazinler gibi çeşitli akıllı malzemeler elde edilmiştir. Bu stratejilerin önemli ve polibenzoksazinlerin benzersiz özellikleri ve avantajlarını dikkate alarak, bu tezde, çeşitli fonksiyonel grupların benzoksazin öncülleri ile kombinasyonu ve elde edilen ürünün özelliklerinin araştırılması üzerinde duruldu.

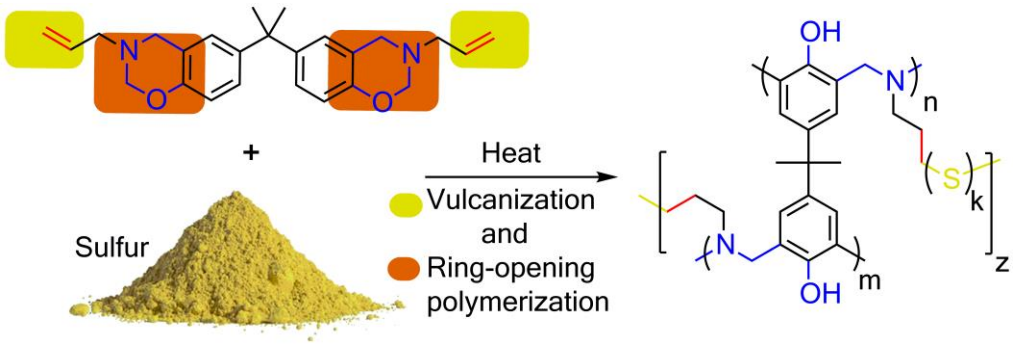
Tezin ilk bölümünde, poli(propilen oksit) içeren benzoksazin unitelerinin supramoleküler etkileşim sonucu kendi kendine iyileşebilmesini sağlayan yeni bir moleküler tasarım geliştirildi. 2000 Da moleküler ağırlığına sahip poli(propilen oksit) bisamin (PPO), 12360 Da moleküler ağırlığına sahip PPO-Benz vermek üzere formaldehit ve bisfenol A ile reaksiyona sokuldu.



Şekil 4 : Karboksilik asit içeren benzoksazin monomeri ve PPO-Benz karışımından kendi kendine iyileşebilen film eldesi.

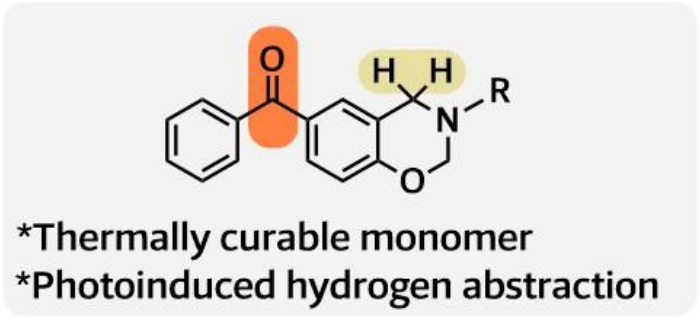
Çapraz-bağlanmış polimer filmler, uygun kompozisyonlarda PPO-Benz ve karboksilik asit içeren benzoksazin monomerlerinin (Carb-Benz), kloroformda çözülerek hazırlanmasıyla, çözücü uçurularak ve 200 °C de benzoksazin gruplarının halka açılma reaksiyonu sonucunda elde edildi. Film ve son ürünün ısısal kürleme ve ısısal kararlılığı incelendi. Bu filmlerin kendini iyileştirme kapasitesinin, formülasyonun içinde Carb-Benz kullanıldığı zaman arttığı gösterildi.

Tezin ikinci bölümünde, yeni bir yaklaşım kullanılarak, alkil fonksiyonel benzoksazin (BA-ala) ve elementel kükürt reaksiyona sokularak, kükürtçe zengin polibenzoksazin kopolimerler elde edildi. Eşzamanlı inverse vulkanizasyon ve benzoksazinlerin halka açma reaksiyonu, belirli oranlarda çözünür kopolimerler oluşturdu. Monomer yapısı ve polimerizasyonda kullanılan oranlar gibi parametreler incelendi. Kopolimerlerin ısısal kararlılığı araştırıldı, termogravimetrik analiz (TGA) ve diferansiyel tarama kalorimetrisi (DSC) kullanılarak saf BA-ala ile türetilen polibenzoksazinle kıyaslandı. Taramalı elektron mikroskobu (SEM) ile malzemelerin yüzey özellikleri incelendi ve elementel kükürt ve benzoksazin kopolimerlerinin mikrometre düzeyinde faz ayrılması olmadan üretilebilirliği doğrulandı. Ayrıca, sünger tipi makro-gözenekli çözünmez polibenzoksazin ağları, 20% kükürt oranında elde edildi.



Şekil 5 : Alkil fonksiyonel benzoksazin (BA-ala) ve elementel kükürtün reaksiyonuyla, kükürtçe zengin polibenzoksazin kopolimerlerin eldesi için yeni bir strateji.

Son olarak, yan zinciri benzoksazin fonksiyonel polibütadienler, fotokimyasal hidrojen ayırma yöntemi ile elde edildi. İlk olarak, yapısında kromoforik karbonil ve hidrojen verici kısımları olan ışığa duyarlı benzoksazin bileşikleri, vanilin veya 4-hidroksibenzofenon kullanılarak geleneksel benzoksazin sentez metoduyla elde edildi. Katkısız polibutadien (PB), benzofenon benzoksazin (BPH ptol) ve vanilin benzoksazin (Van-A) varlığında, 300-350 nm ışık altında aydınlatılarak, zinciri başına yaklaşık 4-5 benzoksazin ünitesi içeren PB oluşturdu. Başarılı modifikasyon, spektral ve ısısal incelemeler ile teyit edildi. Benzoksazin bağlı PB'lerin, herhangi bir katalizör gerektirmeden, termal kürleme ve yüksek yanma verimi ile polibütadien termosetler oluşturduğu gösterildi.



Şekil 6 : Yapısında kromoforik karbonil ve hidrojen verici bölümleri olan ışığa duyarlı benzoksazin bileşiği.

1. INTRODUCTION

High-performance polymers are produced commercially because of wide range applications in various area. Phenolics, epoxies, bismaleimides, cyanates and polyimides are the commonly used thermoset systems. Among these, phenolic resins are the most known members of the systems. In spite of their fascinating features such as dimensional stability, flame and solvent resistance and good mechanical strength, a number of short-comings are related with these thermosets. Poor shelf life, volumetric shrinkage, brittleness, releasing of by-products, corrosions on the equipments are the main short-comings of phenolic resins. Polybenzoxazines were synthesized to avoid these problems and gained a considerable attention in the field of thermosetting polymers. Polybenzoxazines are addition-cure phenolic systems and having outstanding properties which is combines mechanical performance of phenolics and molecular design flexibility. For example, they have near zero-volumetric change on curing and do not need any strong acid catalysts or additives for curing. They provide also high thermal stability and resistance against flame. Other superior properties are good mechanical performance, low water absorption, and high char yield. These features are mainly occasioned by the Mannich base bridges -CH_2-N(R)-CH_2-, the hydrogen bonds between nitrogen and phenolic -OH groups and the cyclic structure of the corresponding monomers. Phenols, amines and formaldehyde are inexpensive and commercially available starting materials for polybenzoxazine synthesis. Vast number of suitable phenolics and primary amines provide molecular design flexibility and as a result, polybenzoxazine resins can be obtain with desired properties (Figure 1.1).

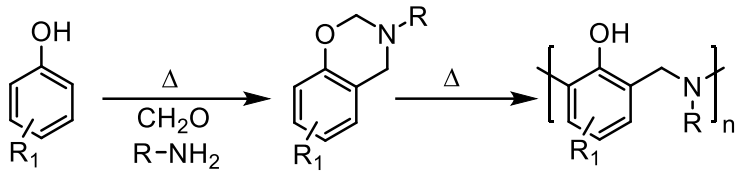


Figure 1.1 : Synthesis of mono-functional 1,3-benzoxazine monomer and **t**hermally activated ring opening polymerization.

1.1 Synthetic Techniques for Benzoxazine Monomers

A six membered heterocyclic oxazine ring with an oxygen and nitrogen attached to a benzene ring forms the benzoxazine structure. Several types of benzoxazine monomers can be synthesized depending on the position of the oxygen and nitrogen in the oxazine ring. Among them, 1,3-benzoxazine (dihydro-2*H*-1,3-benzoxazine) was first synthesized by Cope and Holly in 1940s by a condensation reaction of primary amines with phenol and formaldehyde. Benzoxazine ring's preferentially reactions with free ortho position of a phenolic compound and formation of a Mannich bridge were found by Burke in 1949. Two-step reaction occurs during the 1,3-benzoxazine synthesis; A Mannich reaction and a ring closure reaction of aromatic or primary aliphatic amines, phenolic derivatives and formaldehyde. Reaction of various suitable amines and phenols provides design flexibility and high performance polybenzoxazines can be synthesized. On the other hand, there are some other alternative methods to synthesis 1,3-benzoxazines; (i) starting from salicylaldehydes through salicylaminesmines and ring closing with formaldehyde, (ii) ortho-lithiation of phenols, reaction with $ZnBr_2$ and *N*, *N*-bis[(benzotriazol-1-yl)methyl] and, (iii) 1,3,5-triphenylhexahydro-1,3,5-triazine reaction as active intermediate (Figure 1.2). After the classical Mannich based method, the third method is appeared to be the most convenient one.

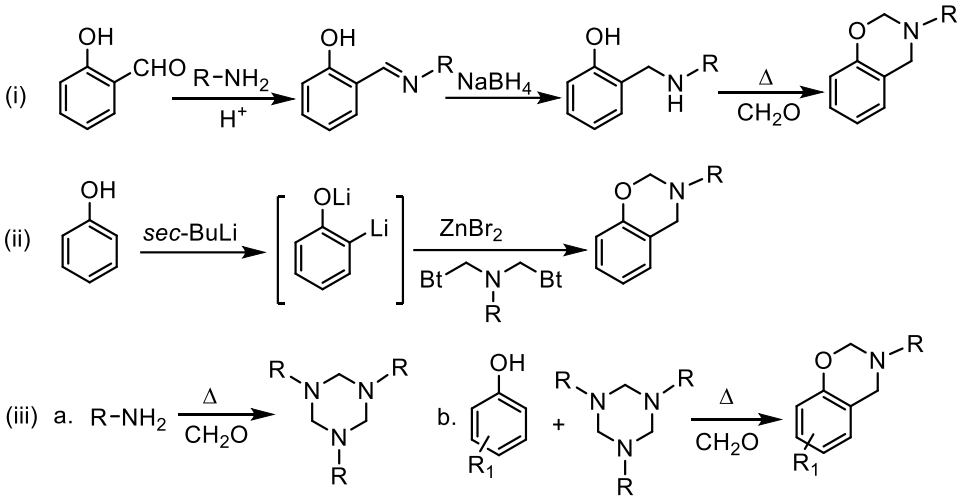


Figure 1.2 : Alternative methods for the synthesis of 1,3-benzoxazines.

1.2 Polymerization Mechanism of Benzoxazines

Due to the distorted structure of oxazine ring, ring-opening reaction can occur under mild conditions. According to the Lewis acid-base definition, high basicity of the oxazine ring supposably make the ring open via a cationic mechanism. The most known curing method is non-catalytic thermally activated ring-opening polymerization. In simple terms, a carbocation forms by the heterolytic cleavage of the bond between N and O atoms. Electrophilic aromatic substitution (Friedel-Crafts reaction) takes place through the *ortho* or *para* position of the phenol after rearrangement of the carbocation. On the other hand, carbocation can attack to the phenolic oxygen to form a phenoxy structure (Figure 1.3). Acidic phenols are known to activate the ring opening reaction of benzoxazines. Phenolic hydroxyls are produced during the polymerization and used as an auto catalyst for the polymerization. The polymerization temperatures vary between 160-260 °C depending on the monomer structure. Although, the reaction being called non-catalytic, it is found that actual reaction is catalytic. Even if pure benzoxazines do not polymerize or polymerize at very high temperatures, impure benzoxazines polymerize at lower curing temperatures.

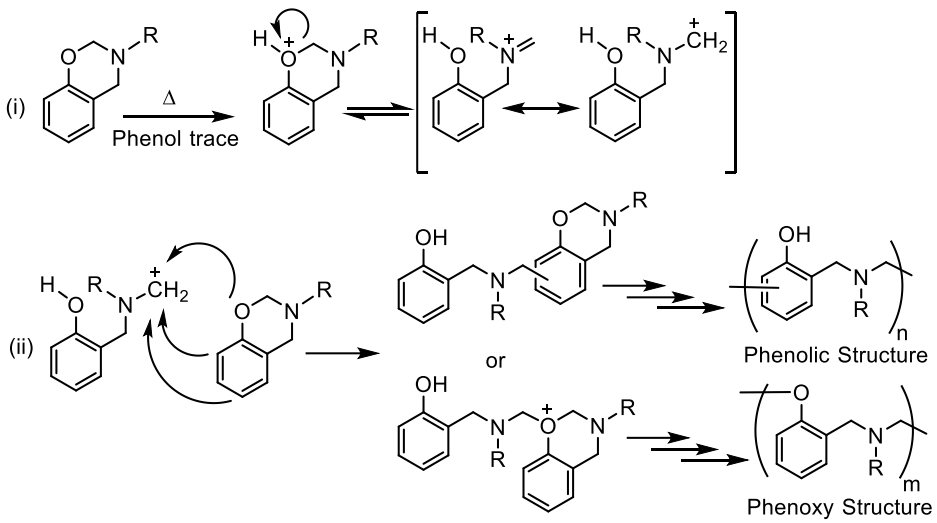


Figure 1.3 : Simplified mechanism of thermal curing of benzoxazines.

Investigations focused on the use of various acids to reduce the high ring-opening temperatures. Influence of acid catalyst on ring-opening polymerization of benzoxazines was investigated by Ishida [1, 2]. Adipic acid has showed good performance compared to the sebacic acid and 2,2'-dihydroxybiphenyl. Acetic acid, p-cresol, trifluoroacetic acid and trichloroacetic have been investigated and it is found that weak carboxylic acids are better than strong carboxylic acids to catalyze the polymerization [3].

Effective initiating systems with several initiators, such as PCl_3, $SbCl_5$, PCl_5, $AlCl_3$, $TiCl_4$, $POCl_3$ were found to yield polybenzoxazines with high char yield [4]. Photoinduced acid generation was proposed as an alternative methodology [5]. Onium salts are used as a photo acid generators (Figure 1.4). Additionally, thiols have been found to reduce ring-opening polymerization temperature.

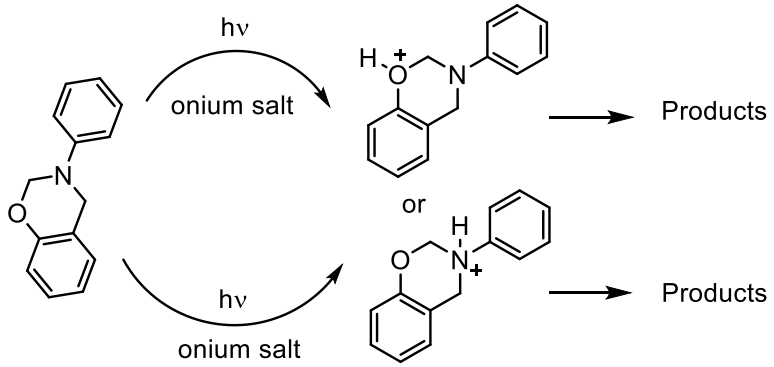


Figure 1.4 : Photochemical activation of benzoxazines.

1.3 Functional Benzoxazines

Benzoxazine resins can be classified as mono-functional, bifunctional, and multifunctional depending on their funtionality. Mono-functional polybenzoxazine generally has low molecular weight, in contrast to the bifunctional polybenzoxazine structure. Thermal degradation of the polybenzoxazines start with the chain breakdown of amin fragments. Thus, linking of various functional group through amine functionality stabilize the Mannich Bridge and improves the thermal stability. Allyl [3], malemide [6], acetylene [2], coumarine [7] and propargyl [8] on the amine group have been found effective to improve thermal stability. Many different benzoxazines were synthesized to control their thermal properties.

1.4 Purpose of the Thesis

The objective of the thesis is to synthesize functional benzoxazine polymers which are bearing different functionality and investigate their properties. Different synthetic strategies are developed and structure property relations investigated. For the characterization of intermediates and final polymers were used analitycal methods such as, chromatographic (GPC), spectroscopic (^{1}H-NMR, UV, FT-IR), thermographic (DSC, TGA) and mechanic (DMA). This thesis is organized in such that each chapter has its own introduction, experimental, results and discussion.

Chapter 2 discusses overall background information about the development of a self-healing approach for poly(propylene oxide)s bearing benzoxazine units (PPO-Benz) through the intra- and intermolecular hydrogen bonding. Solvent casting method is used to obtain cross-linked polymer films. PPO-Benz and carboxlic acid containing benzoxazine monomer (Carb-Benz) were mixed with suitable compositions and followed by thermal curing at 200 °C. Thermal stability of the film were investigated and it was demonstrated that the self-healing capacity of the films was improved by employing Carb-Benz in the formulation.

Chapter 3 shows a novel strategy to obtain sulfur-rich polybenzoxazine copolymers by reacting allyl functional benzoxazine (BA-ala) and elemental sulfur. Simultaneous inverse vulcanization and ring-opening reactions of benzoxazine generated soluble copolymers in specific feed ratios. Parameters such as monomer structure and feed ratios on the polymerization were studied.

Chapter 4 demonstrates the synthesis of side-chain benzoxazine functional polybutadienes by photoinduced hydrogen abstraction process. It is demonstrated that PBs attached with benzoxazines undergo thermally activated curing without any catalyst to form polybutadiene thermoset with high char yield.

Finally, concluding remarks are summarized in Chapter 5 along with recommendations for further work.

2. BENZOXAZINE BASED THERMOSETS WITH AUTONOMOUS SELF-HEALING ABILITY[1]

Polybenzoxazines are relatively new phenolic resins and offer a superior alternative to novolac and resole type systems. Thus, the interest in polybenzoxazines is continuously increasing in the polymer science field as reflected by the scientific publication and patents. Most of the superior properties of these addition-cure resins are stemming from the Mannich base bridges $–CH_2–N(R)–CH_2–$ and the intra and intermolecular hydrogen bonds between phenolic –OH and amine groups. These non-covalent attractions are the reason for the low humidity uptake and high glass transition temperatures (T_g) of these systems. Moreover, upon ring opening polymerization (ROP) the cyclic structure of the monomers generally inhibits shrinkage of the resin which is a common problem for many curable systems. Non-catalytic polymerization, high char yield, limited release of by-products during curing are additional benefits of the polybenzoxazine based resins. The synthesis of polybenzoxazines from its corresponding 1,3-benzoxazine monomers can simply be achieved by thermally activated ROP with or without a catalyst (Figure 2.1) [9]. In non-catalytic conditions the ROP temperatures vary in a range of 160–250 °C [10-14].

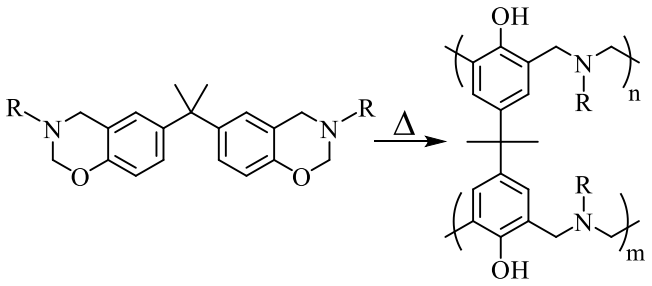


Figure 2.1 : Thermally activated ring opening polymerization of a bisbenzoxazine monomer.

The properties of polybenzoxazines resins can be controlled by three common methodologies that are i) synthesis of monomers, ii) forming their composites by

[1] This chapter is based on the paper, **Arslan M.,** Kiskan B., and Yagci Y., Benzoxazine-Based Thermosets with Autonomous Self-Healing Ability. *Macromolecules*, 48, 1329-1334.

adding fillers or additives and iii) synthesis of polybenzoxazine prepolymers [15-19]. A great number of benzoxazine monomers containing hydroxyl, [20] alkyl, [21] phenyl, [22] maleimide, [6, 23] propargyl, [8] nitrile, allyl, [3] and carboxyl [24] groups were synthesized. The synthesis can easily be facilitated by using suitable phenols, primary amines and formaldehyde as starting materials (Figure 2.2) [25-31].

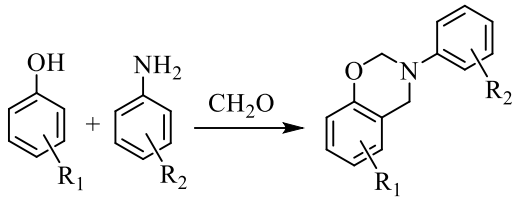


Figure 2.2 : Synthesis of a mono-functional 1,3-benzoxazine monomer from a phenol and a primary amine.

The other widespread approach to regulate the properties is based on the preparation of polybenzoxazine prepolymers [32-39]. Such polymeric precursors generate high crosslinking degree, reduce cold flow and increase the toughness of the resin. Various chemistries were successfully used to synthesize polybenzoxazine prepolymers including coupling reactions, alternating copolymerization of donor-acceptor monomers, [23] Diels-Alder, [40] Mannich reactions, [41] polyesterification, [42] polyetherification, [43] hydrosilylation [44, 45] etc. These synthetic approaches essentially yield diverse polybenzoxazines with designed properties. Although, polybenzoxazines were used in many applications, the use of polybenzoxazines in the synthesis of self-healing materials has scarcely been investigated. In this direction, recent publications from the authors' laboratory reported the first usage of polybenzoxazine precursors as a self-healing additive for polysulfones [46] and coumarin functional polybenzoxazines [47]. In these systems, heat and light induced intrinsic self-healing was accomplished through covalent bond formations. In contrast to such healing mechanism, supramolecular networks that generally associate with reversible supramolecular interactions exhibit a higher dynamic healing behavior. It appears that these materials display autonomous healing upon damage and have numerous potential applications [48, 49]. So far, such self-healing has been reported in clay-dendrimer mixture, [50] metal ion-polymer systems, [51, 52] supramolecular gels, [53, 54] π-π stacking networks, [55, 56] disulfide-thiol exchange [57] and multicomponent systems [58]. Additionally, self-healing polymers based on hydrogen bonding can also generate supramolecular network systems that contain highly dynamic non-covalent bonds. These bonds show

a reversible “sticker-like” behavior enabling connection and reconnection between several hydrogen bonding regions. Typical examples include Ureido-pyrimidone bonding, nucleobases and similar systems, Leibler bond, butylurea of guanosine and 2,7-diamido-1,8-naphtyridine attractions, polystyrene grafted with polyacrylamide and quadruple hydrogen bonding [59]. In the view of supramolecular attraction concept, the intra and intermolecular hydrogen bonding in polybenzoxazines can be utilized to design a novel self-healing system. To demonstrate the feasibility of this strategy, we report poly(propylene-oxide) based polybenzoxazine networks with embedded carboxylic acid containing benzoxazines as the stimuli to form efficient autonomous healing though both covalent and supramolecular network.

2.1 Results and Discussions

In general, the elementary steps of supramolecular self-healing systems are inter-diffusion and entanglement of polymer chains. Accumulation of hydrogen bonding sites on the cut edge, surface approach and wetting are important. For spontaneous repair of material as a response to damage a balanced dynamic system for formation of a network should be chosen. In other words, a sufficiently high molecular flexibility must be established to form dynamic networks. Strong interacting functional groups in the supramolecular system can result in high mechanical stability but at the same time slow down or reduce the healing capacity. Weak interactions enhance molecular dynamics, but in such cases can generate only soft materials that could not meet required mechanical properties. Thus, for efficient healing, we have deliberately selected poly(propylene-oxide) with a molecular weight of 2000 Dalton as the matrix material in polybenzoxazine precursor synthesis so as to introduce sufficient dynamics to the healable system. Such propylene oxide amines have high chain mobility and could provide softness to the networks that they were incorporated [60, 61]. Hence, a successful synthesis of poly(propylene-oxide) based polybenzoxazines (PPO-Benz) were performed using poly(propyleneoxide) bisamine (PPO) (M_n: 2000) and bisphenol-A as difunctional phenol source (Figure 2.3). Toluene/ethanol mixture (2:1, v:v) was used as the solvent in order to prevent possible gelation during precursor synthesis [33]. It is known that depending on the solvent used, formaldehyde with primary amines can readily forms 1,3,5-dihydrotriazines.

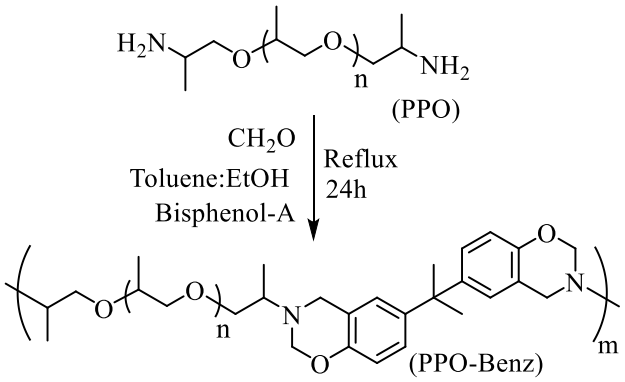


Figure 2.3 : Synthesis of benzoxazine containing poly(propylene oxide)s (PPO-Benz)s.

The chemical structure of the PPO-Benz was confirmed by ^{1}H-NMR and FT-IR spectral analysis. As can be seen from Figure 2.4 where ^{1}H-NMR spectrum of PPO-Benz is presented, the appearance of the protons resonating at 4.92 (O-C**H$_2$**-N) and 4.01 ppm (Ar-C**H$_2$**-N) is clear evidence for the benzoxazine ring formation on poly(propylene oxide). Moreover, the peak at 1.59 (-C**H$_3$**) disclose the bisphenol A moiety. The integration ratios of the characteristic peaks agree with the proposed structure. FT-IR spectra of the correponding polymers also give evidence for the formation of benzoxazine functional PPO-Benz precursor (Figure 2.5). The consumption of amino groups of poly(propylene)amines can be detected by the disappearances of N-H stretching vibrations in the spectra. Moreover, the stretching vibrations of aromatic C-H (3022-3055 cm-1) and aromatic C=C (1511-1621 cm-1), the out of plane bending vibrations of aromatic C–H at 963 cm^{-1} are detected for the precursor obtained. These results confirm successful synthesis of benzoxazine functional poly(propylene oxide).

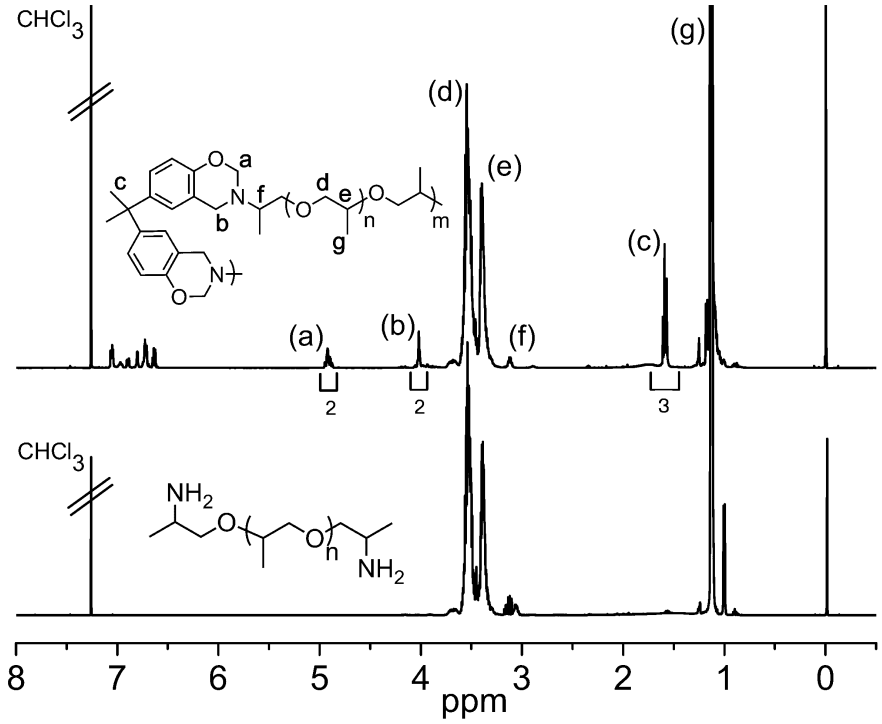


Figure 2.4 : ^{1}H NMR spectra of PPO and corresponding PPO-Benz.

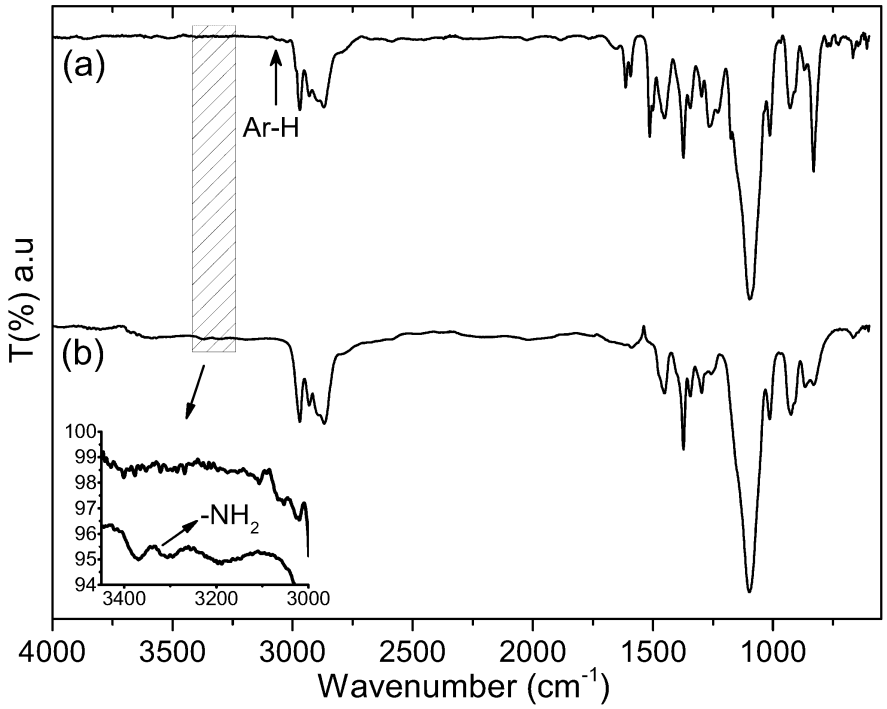


Figure 2.5 : FT-IR spectra of PPO-Benz (a) and PPO (b).

The GPC trace of the precursor polymer is depicted in Figure 2.6. Clearly, successive condensation reactions resulted in the formation of PPO with relatively high

molecular (M_n = 12360 g mol^{-1}, PDI = 1.43). The shoulders observed in the lower molecular weight region are typical consequences of the step-growth polymerization.

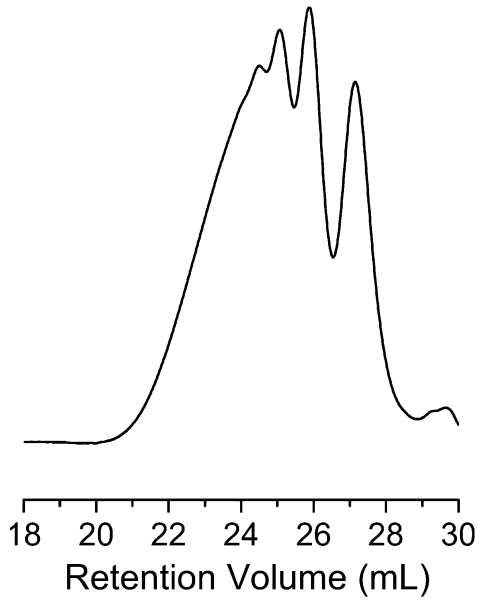


Figure 2.6 : GPC trace of PPO-Benz precursor.

It is known that depending on the functionalities present, benzoxazines have the ring opening polymerization temperature generally between 150-260 °C. Figure 2.7 shows the DSC profile of PPO-Benz. The precursor is curable and its curing temperature is in accordance with many classical bisbenzoxazine monomers or main chain polybenzoxazine precursors. PPO-Benz showed an exotherm with an onset at 221 °C, end-set at 271°C and the curing maximum was detected as 252 °C. The total amount of curing exotherm is 20 J/g. After curing of PPO-Benz, the second run did not exhibit any curing exotherm indicating the consumption of the benzoxazine groups in the first thermal treatment. Glass transition temperature (T_g) of polybenzoxazine films were detected by DSC with a fast scanning method (40°C/ min.). Two T_g s were observed at 32 and 151 °C, respectively. These values reveal two distinct domains in a typical film.

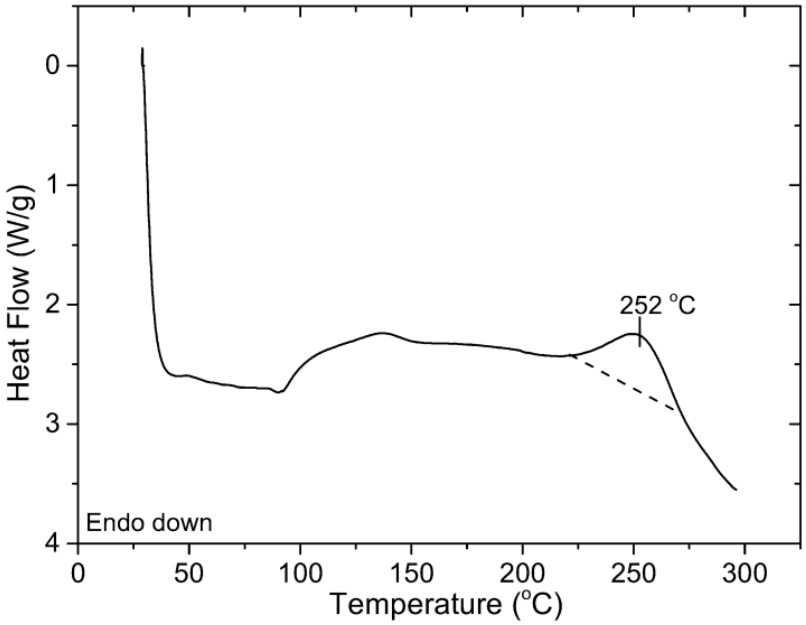


Figure 2.7 : DSC thermogram of PPO-Benz under N_2 atmosphere.

Autonomous healing of thermally cured PPO-Benz polymer films was investigated. For this purpose, the films were prepared first by mixing PPO-Benz and Carb-Benz with the structure presented in Figure 2.9 in three different w/w ratios 1:0.1; 1:0.05; 1:0.025. The abbreviations Carb-Benz10%-PPO-Benz, Carb-Benz5%-PPO-Benz and Carb-Benz2.5%-PPO-Benz represents the respective mixing ratios. The maximum weight of Carb-Benz kept 100 mg in one gram of PPO-Benz, because excess amount of Carb-Benz generates voids in the film and phase separation takes place. While the onset of the ring opening reaction of pristine PPO-Benz is 221 °C (Figure 2.7), the curing is conducted at 200 °C, because ring-opening polymerization of Carb-Benz commences at around 160 °C (See Figure 2.7) and triggers the curing of PPO-Benz easily. In principle, the films could heal themselves without an external stimulant through hydrogen bonding with the existing amino phenols. However, only inefficient healing was attained without addition of Carb-Benz. A possible drawback of carboxylic acid group could be decarboxylation of acid groups, it has been reported[19] that the weight loss at around 300 °C increases with the carboxylic benzoxazine content. We have also observed this effect for the film which was prepared with the ratio of 1:0.1 (w/w) as the bubbles were formed after curing. However, the films with less amount of Carb-Benz were smooth. (Figure 2.8)

Figure 2.8 : Photograph of cured Carb-Benz10%-PPO-Benz (a) and cured Carb-Benz%5+PPO–Benz (b).

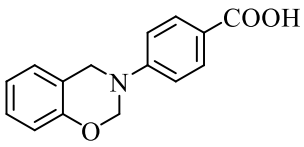


Figure 2.9 : The structure of Carb Benz.

Basically, healing of a polymeric material can be regarded as the recovery of its properties and polymers exhibit various properties that can be a measure of the extent of healing. In general, recovery of the properties such as tensile strength, fracture toughness etc. is measured to quantify the extent of healing. However, such quantification could not reflect the exact amount of the recovery, since pure mechanical properties cannot cover the overall properties of a material. Even though, in practical manner measuring the degree of healing of polymeric systems for a defined mechanical property is commonly used as the basic method. Accordingly the "healing efficiency" of a self–healing system the can be expressed as η;

$$\eta = 100\ x\ \frac{K_{healed}}{K_{virgin}} \qquad (2.1)$$

where K_{healed} and K_{virgin} are the fracture toughness (the area of stress–strain curve) of the healed and virgin specimens, respectively. Thus, tensile tests were performed to measure the ability of the damaged cured Carb-Benz and PPO-Benz mixture (Carb-Benz+PPO-Benz) to recover their strength. To do so, the damage generated by cutting the film into two separate parts. Then, the damaged specimens were kept in contact from the edges of the cut with applied pressure using a glass slip for 12 h at

ambient temperature. Thereafter, the healed specimens were subjected to tests for healing efficiency and the ratio of tensile strengths of the healed and virgin specimens were found. Figure 2.10 shows that tensile strengths of cross–linked films of Carb-Benz+PPO-Benz mixtures can be restored to some extent and the efficiency of the healing for cut specimens are tabulated in Table 2.1. A visual demonstration of the recovery is presented in Figure 2.11 and a video as supplementary material is present.

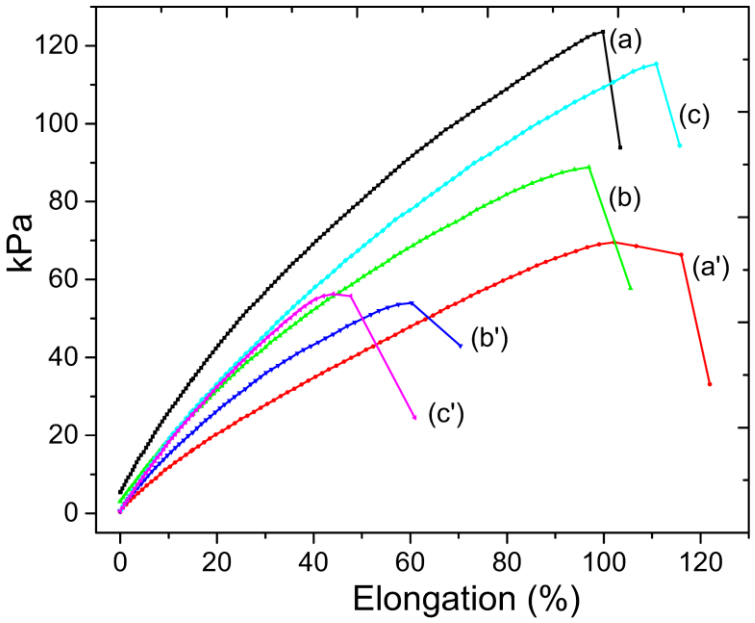


Figure 2.10 : Stress–Strain (%) behavior of virgin specimens Carb-Benz%10+PPO–Benz (a), Carb-Benz%5+PPO–Benz (b), Carb-Benz%2.5+PPO–Benz (c), cut healed specimens (a'), (b'), (c'), respectively.

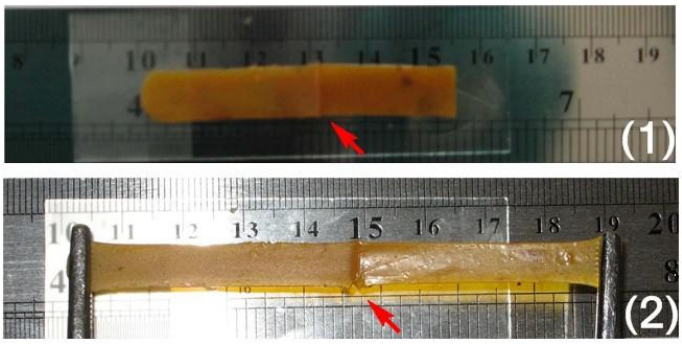


Figure 2.11 : Photograph of cut healed specimen (1) and stretching of the same sample (2) (Carb-Benz%5+PPO–Benz).

Table 2.1 : The efficiency of the healing for cut specimens.

Polymer	Young Modulus (*E*) (kPa)	Healing Efficiency (η)(%)
CarbBenz%10+PPO-Benz	182.3	96
*CarbBenz%10+PPO-Benz	96.4	
CarbBenz%5+PPO-Benz	163.7	41
*CarbBenz%5+PPO-Benz	157.5	
CarbBenz%2.5+PPO-Benz	136.5	26
*CarbBenz%2.5+PPO-Benz	190.1	

*Cut healed sample

In polybenzoxazines, two types of hydrogen bonding can be considered; (i) intermolecular hydrogen bonding between two phenolic hydroxyl groups of polybenzoxazine and (ii) intramolecular hydrogen bonding between phenolic hydroxyl groups and nitrogen atoms on the Mannich Bridge. These hydrogen bonding attractions can easily be detected in IR spectrum of polybenzoxazines as broadening of phenolic O-H stretching vibration band. Addition of Carb-Benz into PPO-Benz during film formation could generate increased number of hydrogen binding sites (Figure 2.12). Binding of -COOH to phenolic –OH and tertiary amine would affect the hydrogen bonding in polybenzoxazine resin and results in a shift of –OH band towards low energy region in IR. Likewise, this shift is clearly detectable in Figure 2.13, evidencing the supramolecular healing mechanism. As stated previously, without addition of Carb-Benz, sufficient healing was not observed indicating the importance of hydrogen bonding for successful healing.

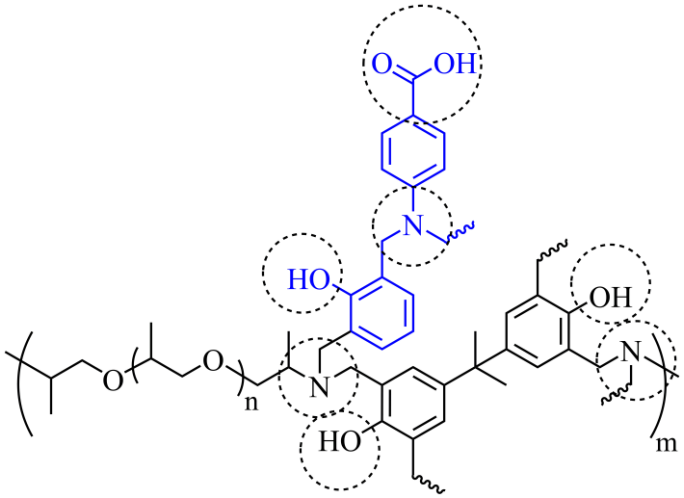


Figure 2.12 : Demonstration of possible hydrogen bonding sites highlighted as circles in Carb-Benz added PPO-Benz network.

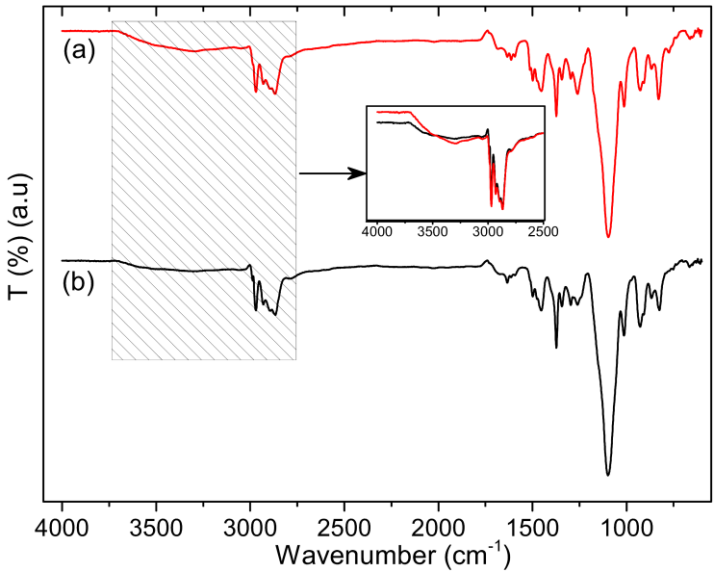


Figure 2.13 : FT-IR spectra of cured Carb-Benz5%-PPO-Benz film (a), cured PPO-Benz film (b).

Thermal stability of the PPO-Benz polymers was explored by thermo gravimetric analysis (TGA) under N_2 atmosphere. The TGA and derivative TGA curves of the cured PPO-Benz and Carb-Benz+PPO-Benz are shown in Figure 2.14 and the results are tabulated in Table 2.2. Carb-Benz+PPO-Benz exhibited slightly higher degradation temperatures of $T_{5\%}$, $T_{\%10}$, T_{max} than PPO-Benz polymers due to the increased the total aromatic content of the film arising from the addition of aromatic monomer. Accordingly, all films almost completely vaporized at 800 °C.

Table 2.2 : Thermal properties of the [a]cured PPO-Benz films.

Film	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	T_{max} (°C)
PPO-Benz	310	335	391
Carb-Benz5%+PPO-Benz	326	345	395

[a]Curing was performed in TGA at 220 °C for 15 min. under N_2 stream (200 mL/min.), $T_{5\%}$: The temperature for which the weight loss is 5%, $T_{10\%}$: The temperature for which the weight loss is 10%, T_{max}: The temperature for maximum weight loss.

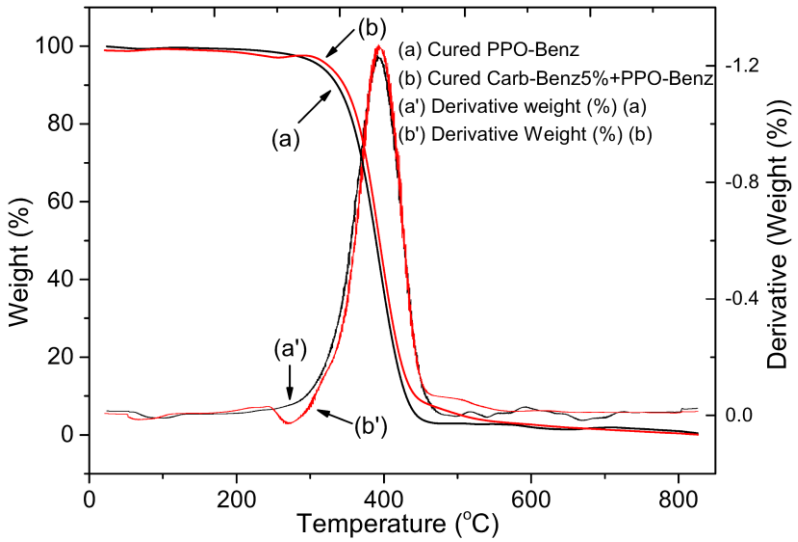


Figure 2.14 : TGA and derivative TGA of cured PPO-Benz (a), (a') and cured Carb-Benz5%+PPO-Benz (b), (b').

2.2 Experimental

2.2.1 Materials

4,4'-isopropylidenediphenol (bisphenol A) (Aldrich, 97%), paraformaldehyde (Acros, 96%), poly(propylene glycol) bis(2-aminopropyl ether) (M_n ~2000 Da, Aldrich), 4-aminobenzoic acid (≥99%, Aldrich), ethanol (≥99.5%, Aldrich), toluene (Carlo Erba, 99.5%), chloroform (Acros, 99+%), hexane (Aldrich, 95%), 1,4-dioxane (Riedel-de Haen 99.5%) and diethylether (≥98%, Aldrich), were used as received.

2.2.2 Characterization

^{1}H NMR spectra were recorded in $CDCl_3$ with $Si(CH_3)_4$ as internal standard, using a Bruker AC250 (250.133 MHz) instrument. FT-IR spectra were recorded on a Perkin-Elmer FT-IR Spectrum One spectrometer. Differential Scanning Calorimetry (DSC) was performed on Perkin–Elmer Diamond DSC from 30 °C to 320 °C with a heating

rate of 20 °C min. under nitrogen flow. Thermal gravimetric analysis (TGA) was performed on Perkin–Elmer Diamond TA/TGA with a heating rate of 10 °C min under nitrogen flow. Molecular weights were determined by gel-permeation chromatography (GPC) instrument equipped with Waters styragel column (HR series 2, 3, 5E) with THF as the eluent at a flow rate of 0,3 ml/min and a Waters 410 Differential Refractometer detector. Uniaxial elongation measurements were performed on polymeric film samples (approx. 16.4 mm length and 8.6 mm^2 cross-section area). Measurements were carried out using a Perkin Elmer Pyris Diamond DMA (SII Nanotechnology Inc.) at 25 °C under 50 mN/min. load speed. The tensile strength and percentage elongation at break were recorded.

2.2.3 Synthesis of poly(propyleneoxide)benzoxazine (PPO-Benz)

In a 250 mL round bottomed flask, paraformaldehyde (10.0 mmol, 0.30 g), bisphenol A (2.6 mmol, 0.60 g) and poly(propylene oxide) bisamine (PPO) (2.5 mmol, 5 g) were dissolved with 50 mL of toluene and 25 mL of ethanol mixture. The reaction mixture was refluxed for 24 hours. The solvent was evaporated under vacuum and a blondish oily product was precipitated in cold *n*-hexane. The precipitation process has been done two times. Final oily product was dried at room temperature in a vacuum for 1 day.

2.2.4 Synthesis of carboxyphenylbenzoxazine (Carb-Benz)

Carb-Benz was synthesized according to the procedure in literature: [62] In a 500 mL round bottomed flask, paraformaldehyde (105.0 mmol, 3.2 g), phenol (53.0 mmol, 5 g) and 4-Aminobenzoic acid (51.0 mmol, 7 g) were dissolved in 200 mL of 1,4-dioxane and refluxed for 5 days. After cooling at room temperature, the solvent removed at reduced pressure. Ethyl ether (150 mL) was added to the oil with magnetic stirring, and a yellow precipitate was obtained. The yellow solid was filtered and dried under reduced pressure. For spectral and thermal characterization data please see Figure 2.15, 2.16 and 2.17.

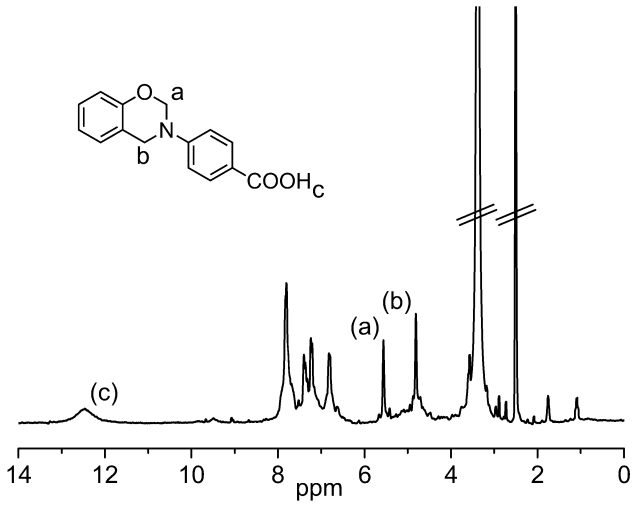


Figure 2.15 : ^{1}H NMR spectrum of Carb-Benz.

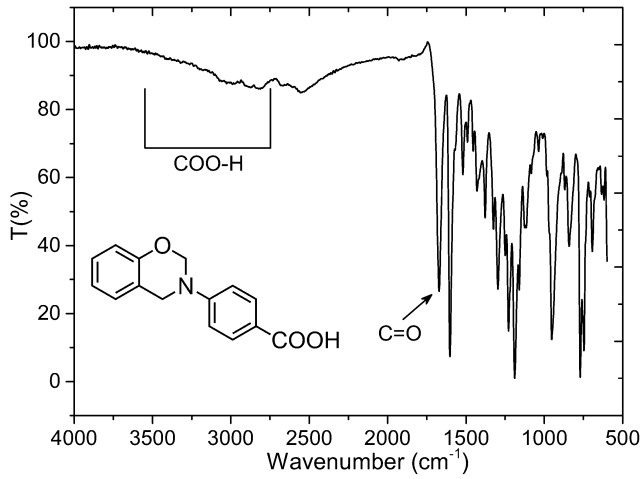


Figure 2.16 : FT-IR spectrum of Carb-Benz.

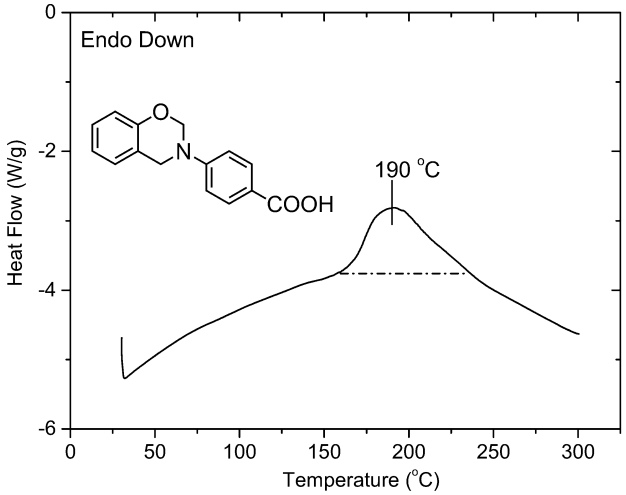


Figure 2.17 : DSC thermogram of Carb-Benz.

2.2.5 Film preparations

To obtain polybenzoxazine films, PPO-Benz was mixed with Carb-Benz monomer in $CHCl_3$ in three different w/w ratios 1:0.1; 1:0.05; 1:0.025. These solutions were charged into a Teflon mold. The solvent was evaporated at room temperature for 5 days. After the solvent removal, films were exposed to thermal curing at 200 °C for 1 h in oven. Finally brownish, transparent polybenzoxazine cross-linked films were obtained.

2.3 Conclusion

The results presented in this paper demonstrate that it is possible to take advantage of hydrogen bonding present in polybenzoxazine networks for autonomous self-healing processes. In the approach, benzoxazine bearing poly(propylene oxide) (PPO-Benz) prepared through conventional main chain polybenzoxazine precursor synthesis methodology using poly(propylene oxide) amines, bisphenol A and formaldehyde. Carboxylic acid containing benzoxazine monomer mixed with PPO-Benz, the film prepared from these components at suitable composition were then cross-linked by thermally activated ring opening reactions of the benzoxazine groups. The autonomous self-healing property of the film was demonstrated on the cured films. Current work is devoted to the design and production of self-healable polymers containing polybenzoxazine networks by supramolecular attractions. The process is useful for further expanding the use of benzoxazines in high performance materials and the chemistry shown here may be extended to other polymers apart from poly(propylene oxide)s.

3. COMBINING ELEMENTAL SULFUR WITH POLYBENZOXAZINES VIA INVERSE VULCANIZATION[2]

High-performance polymers are produced commercially and have wide-range of applications in various areas such as aerospace, adhesives, structural materials, electronics and paints [63]. In general, thermosetting polymers namely, phenolics, epoxies, bismaleimides, cyanate esters, vinyl esters and polyimides are being used [64]. Among them, phenolic resins (novolac and resole) are the best known members of the thermosetting family. Although these resins are widely used for various purposes due to their many superior properties, they exhibit some drawbacks such as shrinkage and release of byproducts during curing and brittleness of end-products [65]. Thus, as an alternative a new type of addition-cure phenolic system, polybenzoxazines, has been developed. Polybenzoxazines are synthesized from 1,3-benzoxazines (dihydro-2H-1,3-benzoxazines) which are six-membered heterocyclic compounds composed of an oxazine ring, with oxygen and nitrogen, attached to a benzene ring [66]. These compounds were first synthesized by Cope and Holly in 1940s [67]. The synthesis of 1,3-benzoxazines is a two-step reaction including a Mannich and a subsequent ring closure reaction by using primary amines with formaldehyde and phenol (Figure 3.1). Owing to the vast number of suitable phenols or related structures and primary amines, an enormous number of benzoxazines can be designed and desired properties can easily be integrated into the final polybenzoxazine resin [10, 22, 31, 39, 68-72]. These resins are synthesized by the polymerization of benzoxazine monomers proceeding through a cationic mechanism which can be performed with or without a catalyst or curative just by heating the monomer up to 150–250 ˚C (Figure 3.1) [5, 73, 74]. Reportedly, the reaction is being called non-catalytic ring opening. However, it is also found that extremely pure benzoxazines do not polymerize or polymerize only at high temperatures over 300 ˚C [75]. On the contrary, benzoxazines with phenol impurities have lower curing

[2] This chapter is based on the paper, **Arslan M.,** Kiskan B., and Yagci Y., Combining Elemental Sulfur with Polybenzoxazines via Inverse Vulcanization. *Macromolecules*, 49, 767−773.

temperatures [25, 76]. These findings indicate the importance of residual phenols from monomer synthesis, accordingly. Thus, the actual process is catalytic and the term non-catalytic reaction refers the systems that are free from added catalyst.

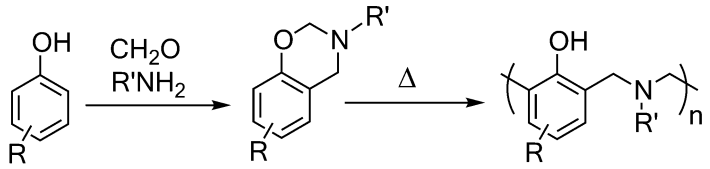


Figure 3.1 : Synthesis of a mono-functional 1,3-benzoxazine from a phenol, primary amine, formaldehyde and corresponding polybenzoxazine.

Generally, most of the polybenzoxazines combine thermal and mechanical strength of phenolics along with vast molecular design flexibility that overcome several short-comings of conventional phenolic resins, while retaining their benefits. Thus, polybenzoxazines gained an immense interest in the field of high-performance polymers. The striking properties of polybenzoxazines are the resistance against flame, [42, 77] high char yield, [78-80] low water absorption, [81, 82] high mechanical strength, [83, 84] high glass transition temperatures (T_g), [85-87] no or limited shrinkage [88] and by-product formation during curing. These properties mainly stem from the Mannich base bridges –CH_2–N(R)–CH_2– and the hydrogen bonds between nitrogen and phenolic –OH groups in the structure [89]. Volumetric shrinkage upon curing is the direct consequence of cyclic molecular structure of oxazine and intra-, inter-molecular hydrogen bonding. However, polybenzoxazines, especially formed from mono-functional benzoxazine monomers, still have the disadvantages of resole and novolac type phenolics such as brittleness and difficulty in processing. Moreover, for many benzoxazines, high cure temperatures (200 ˚C or higher) are detected as another drawback. Several strategies have been applied to overcome these limitations including; (i) monomer modification by incorporating various functionalities, [7, 26, 29, 43, 90-96] (ii) synthesis of main-, side- or end-chain polybenzoxazine precursors [15, 17, 18, 37, 41, 46, 47, 80, 97, 98] and (iii) mixing polybenzoxazines with another polymer or filler [16, 39, 62, 99-102]. The third approach can be extended to reactive fillers such as elemental sulfur. Since, elemental sulfur is melt processable and can generate radicals on S atom during heating and have ability to react with double bonds seen in vulcanization of poly(butadiene)s. Furthermore, the costs of such processes are relatively low because sulfur is the third most abundant element in fossil fuel after carbon and hydrogen. It

is obtained in vast amounts as a by-product of natural-gas and petroleum refining operations. The majority of the sulfur is stored as massive deposits in remote areas for the reason of its limited usage in chemical industry. Today, sulfur is mainly used in the production of sulfuric acid [103]. Some other applications are currently being developed for expanding the use of sulfur. For example, sulfur is used as cathode material for rechargeable batteries, including lithium–sulfur (Li–S) [104] and sodium–sulfur (Na–S) [105, 106] systems. Materials with high refractive indexes can be synthesized from sulfur bearing functional groups [107]. Sulfur rich materials also exhibit high transparency in the IR region, which enables their application in IR optical materials [108]. Sulfur has also pesticidal properties and is used in agricultural industry [109-111]. Moreover, relatively weak S-S bond has been utilized in dynamic covalent chemistry [112, 113].

A recent application of sulfur is the treatment of molten sulfur with diisopropenylbenzene affording stable polymeric materials at a temperature above 180 ˚C [114]. The stability of such polymers was high even at a very high sulfur content of over 90%-wt and did not revert to elemental sulfur upon standing as it is know that pristine polysulfide auto-decomposes to lower molar mass cyclic sulfurs. The reaction of elemental sulfur with divinylic monomers were called as “inverse vulcanization” and scaled up to the kilograms [115-118]. These copolymers exhibited excellent IR transparency and high refractive indices, and could readily be processed into free-standing lenses [108]. Besides, the dynamic covalent properties of S-S bonds were also observed in such polymers and they could be used as thermally healable optical polymers for mid-IR thermal imaging applications. By this way, damaged lenses and windows from these materials were reprocessed to recover their IR imaging performance [119]. As part of our continuous interest in developing new chemistries for benzoxazine based systems to expand their applications, herein we report a simple and efficient method for the preparation of high sulfur containing polybenzoxazines by using inverse vulcanization chemistry. Allyl functional benzoxazines were synthesized and reacted with molten sulfur for this purpose. The sulfur loading capacity and thermal characteristics of the resulting sulfur-polybenzoxazine copolymers were also determined.

3.1 Results and Discussion

As stated in the introduction part, polysulfides are thermodynamically unstable at room temperature and slowly revert to cyclooctasulfur (S_8). Thus, the direct use of these polymers for material applications is uncommon. However, combination of elemental sulfur with vinylic structures through a radical process advanced sulfur based materials. There are various vinylic monomers present and can be utilized in this direction. It seemed, therefore, appropriate to replace vinylic systems with allyl containing benzoxazines form the corresponding copolymers. For this purpose, an allyl functional bisbenzoxazine (BA-ala) was synthesized using allyamine, bisphenol A and formaldehyde according to the reported procedure [3, 44, 45] (Figure 3.7). The structure of the BA-ala obtained was characterized by spectral analysis (see Figures 3.2 and 3.3).

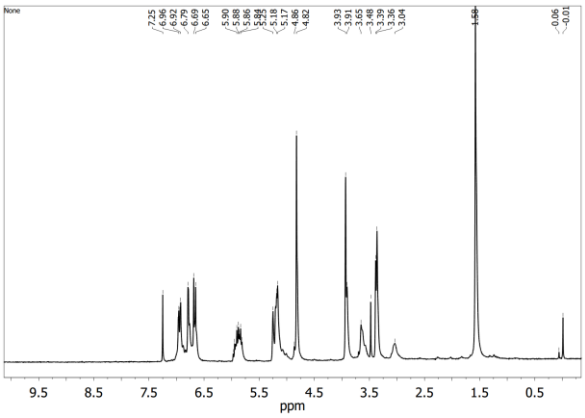


Figure 3.2 : ^{1}H NMR spectrum of BA-ala.

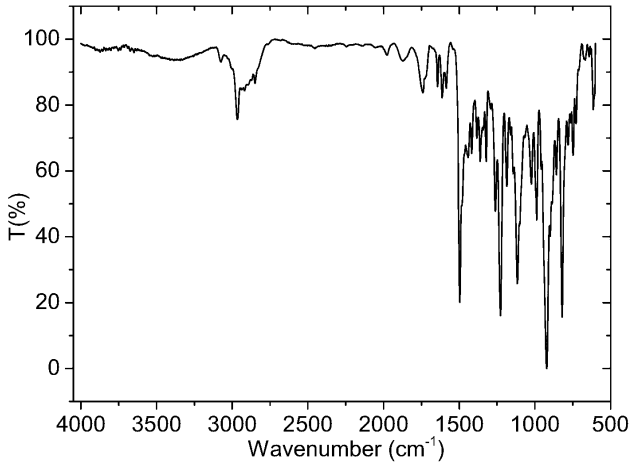


Figure 3.3 : FT-IR spectrum of BA-ala.

Sulfur based copolymers were prepared by heating the mixture of BA-ala and elemental sulfur in various amounts (Figure 3.7). The allyl groups of BA-ala react

with sulfur radical and C-S covalent bond are formed between benzoxazine unit and polysulfide moiety. In the meantime, ring-opening of the oxazine takes place producing polybenzoxazine. In this way, polysulfide is stabilized with polybenzoxazine bridges to give a copolymer (abbreviated as poly(BA-ala-*co*-sulfur)). A blank experiment was performed in order to get more insight for the radical reaction between S_8 and ally moiety of BA-ala. In this experiment, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (25%-wt) was added as a radical scavenger into the S_8 (25%-wt), BA-ala (50%-wt) mixture to cease the radical reactions consequently preventing copolymer formation. Remaining allyl moieties were also detected by FT-IR spectroscopy. Allylic =C–H, C=C stretching vibrations at 3050 and 1652 cm^{-1}, respectively, are visible (Figure 3.4).

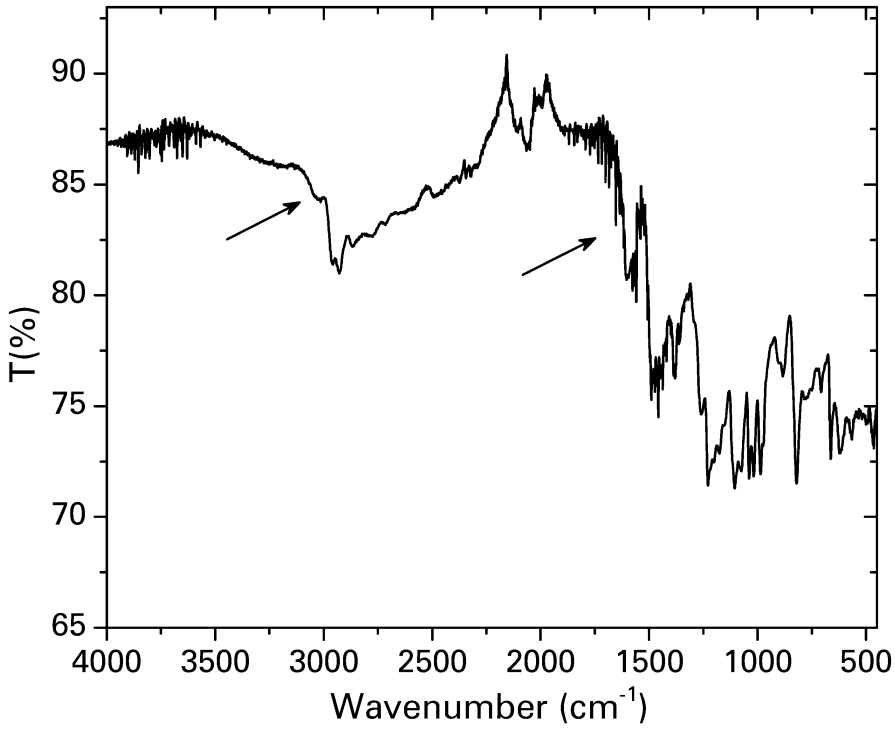


Figure 3.4 : FT-IR spectrum of blank experiment (2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (25%-wt) was added as a radical scavenger into the S_8 (25%-wt), BA-ala (50%-wt)).

Moreover, a monofunctional benzoxazine from phenol, benzylamine (P-Bza) [21] is used instead of allyl functional benzoxazine with a 0.5 mass ratio of P-Bza to S_8 to eliminate a possible role of oxazine functionality in the copolymerization. The result of this experiment showed that P-Bza crosslinked within itself and S_8 remained unreacted. Reactions without added TEMPO gave copolymers that are mostly soluble in various solvents and could be characterized by NMR spectroscopy and

GPC. The high solubility of the polymers can be considered very unusual for a curable system and it is known that even mono-functional benzoxazines produces networks upon curing. However, the amount of sulfur plays an important role in the solubility since polymers with low amounts of sulfur is insoluble. It appears that the mass of polysulfide and elemental sulfur during the reaction do not allow benzoxazine monomers to encounter efficiently to produce a network. This effect is so dominant that even the acidic conditions occurred during the reaction is not enough for a network formation. The acidity of the reaction was checked simply by a litmus paper. As it is known, acids facilitate ring opening reaction and can trigger premature opening of the oxazine ring resulting in a reduction in curing temperature as demonstrated by DSC studies [120]. The acidic medium can be associated with gas formation during the reaction, which is probably H_2S. An experiment was designed to further confirm the gas release and its nature. Thus, the released gas was reacted with Ag^+ in 1 M $AgNO_3$ solution by using a suitable set-up connecting two glass vessels through a plastic tube (Figure 3.5). Upon heating, the formed gas instantly reacted with and Ag^+ ions which was accompanied by formation of a black precipitate or colloidal dispersion of Ag_2S, indicating H_2S release. (Figure 3.5(b)).

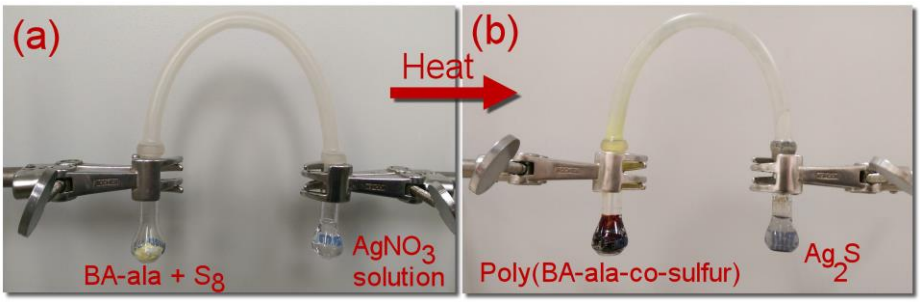


Figure 3.5 : Images of before (a) and after (b) the reaction and the set-up used to trap the released gas.

On the other hand, the gas release during copolymerization resulted in macroporous end-structure when benzoxazine monomer is used in excess such as 80% BA-ala (w/w) (Figure 3.6).

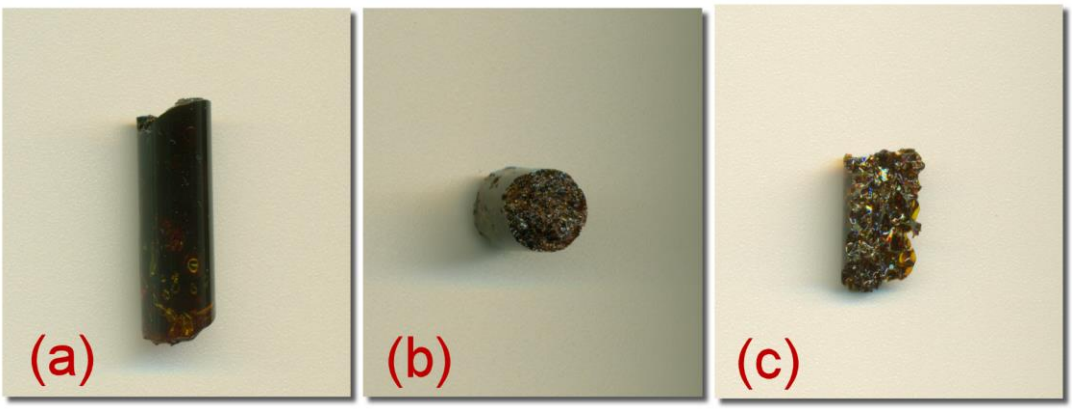


Figure 3.6 : Images of poly(BA-ala-co-sulfur) with 20%-wt S_8 feed ratio. Horizontal (a), vertical (b) and inner (c) views of the crosslinked material.

Owing to the voids formed, insoluble resin exhibit low mechanical strength compared to pristine polybenzoxazine resins, even the material can be broken into parts by hand. However, such a sponge-like morphology is advantageous for applications demanding high mass transport, like catalyst, adsorption, and extraction science. Thus, an easy method for these distinct materials is also reported.

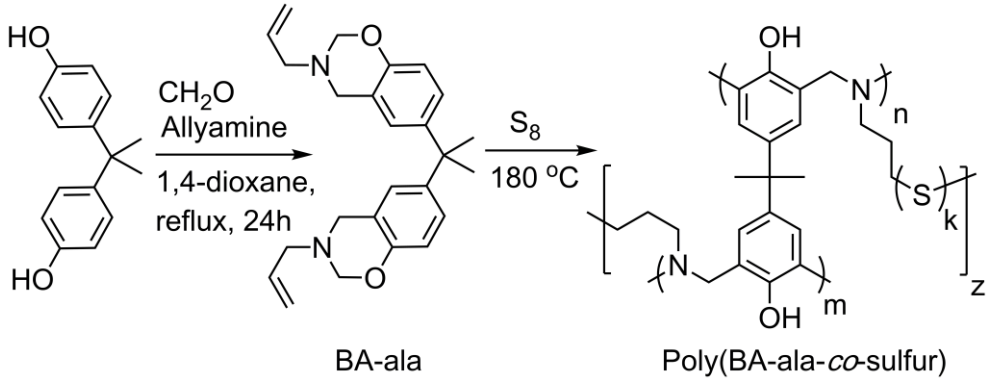


Figure 3.7 : Synthesis of BA-ala and sulfur copolymer poly(BA-ala-*co*-sulfur).

All the copolymers were soluble in THF in particular S_8 feed ratios and molecular weight characteristics could be analyzed by GPC against polystyrene standards. Clearly, successive polymerization reactions resulted in the formation of copolymers with relatively high molecular weights. The GPC traces (Figure 3.8 and 3.9) showed bimodal molecular weight distribution with relatively high polydispersities as a consequence of the characteristics of step-growth polymerization and two different reactions proceeding in the system.

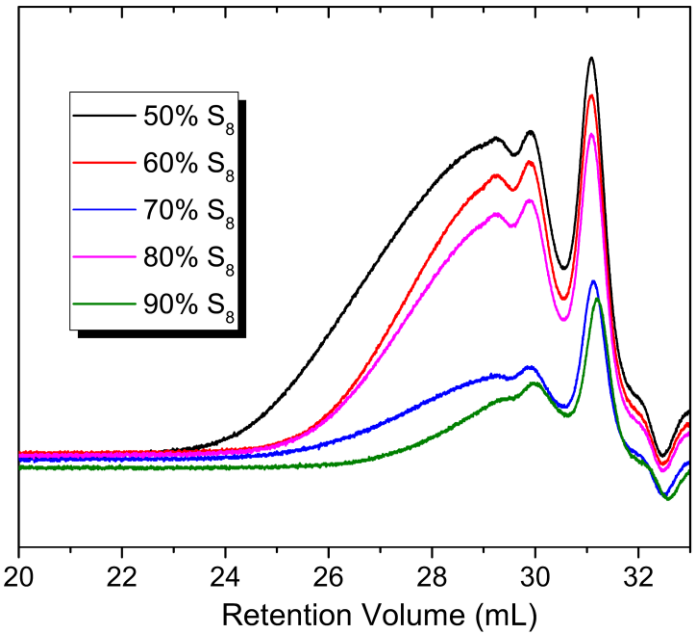


Figure 3.8 : GPC traces of poly(BA-ala-co-sulfur)s obtained by using refractive index (RI) detector. The bands at ca. 31.5 mL belong to butylated hydroxytoluene (BHT).

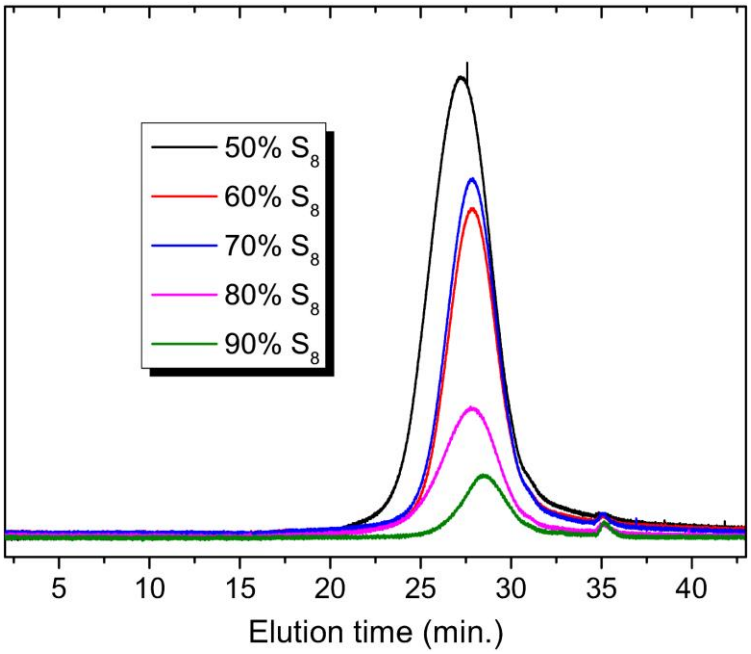


Figure 3.9 : GPC traces of poly(BA-ala-co-sulfur)s obtained by using light scattering (LS) detector.

According to GPC data, with the increasing S_8 amount in the reaction mixture, the molecular weights of the copolymers obtained grew consistently. The molecular weight characteristics are tabulated in Table 3.1.

Table 3.1 : Molecular weight characteristics of the poly(benzoxazine-*co*-sulfur)s in various S_8 amounts determined by GPC according to polystyrene standards.

S_8 feed ratio (%)(w/w)	M_n[a]	M_w[a]/M_n[a]
50	38650	2.50
60	28850	2.94
70	31090	2.64
80	112100	2.76
90	71500	3.39

[a] Obtained by using light scattering detector

As can be seen from Figure 3.10 where ^{1}H NMR spectra of BA-ala and poly(benzoxazine-*co*-sulfur)s with various sulfur amounts are presented, the disappearance of the protons resonating at 5.9 (–C***H***=CH) and 5.2 ppm (–CH=C***H***) is clear evidence for the consumption of ally moiety by sulfur atoms. Moreover, the peaks those appear at 2.5 ppm (–S–C$\boldsymbol{H_2}$–) after copolymerization also support the sulfur addition to allylic groups. The aromatic and –C$\boldsymbol{H_3}$ protons of bisphenol A moiety remain in the copolymers verifying the presence of polybenzoxazine units in the final structures. Moreover, the peak belonging to –N–C$\boldsymbol{H_2}$–O bridge in oxazine ring vanished after the reaction indicating complete ring opening of reaction of benzoxazine. The integration ratios of the peaks do not agree well with the ideal proposed copolymer structure since the polymerization is uncontrolled and polysulfide and polybenzoxazine segments may be formed in a concomitant and/or sequential order and the structure is most probably branched or hyperbranched.

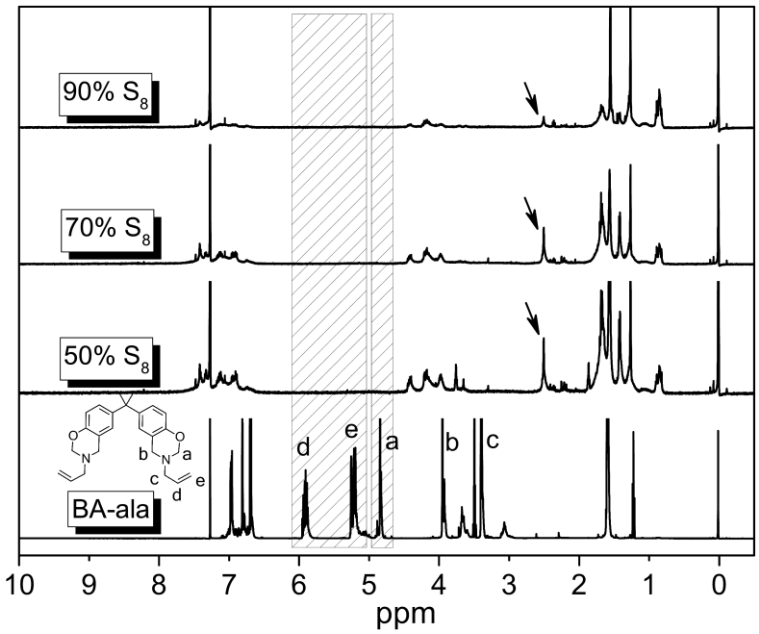


Figure 3.10 : ^{1}H NMR spectra of BA-ala and poly(BA-ala-co-sulfur)s according to their sulfur ratios (w/w). See supporting information (Figure 3.11) for wider scale ^{1}H NMR spectra of copolymers.

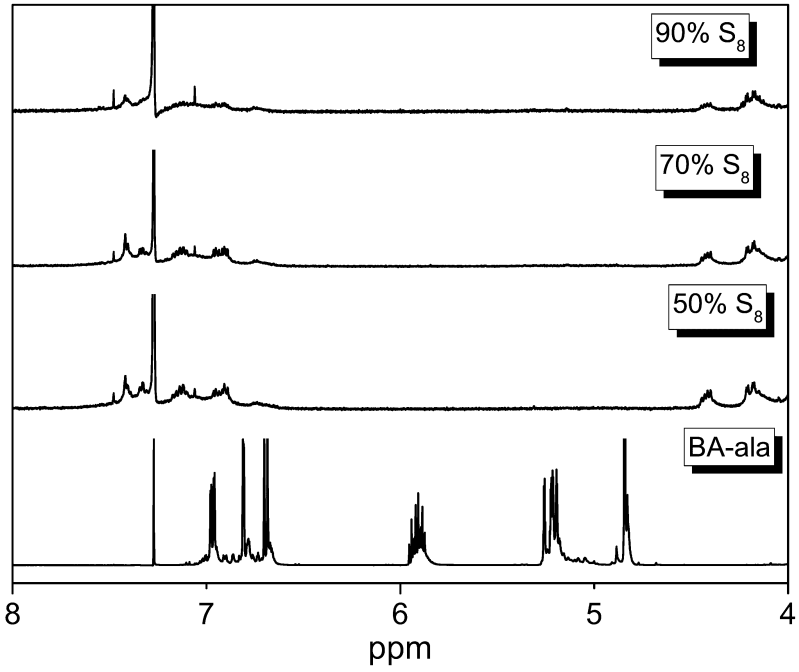


Figure 3.11 : ^{1}H NMR spectra of BA-ala and poly(BA-ala-co-sulfur)s according to their sulfur ratios (w/w).

The overlaid FT–IR spectra of the corresponding copolymer and BA-ala also give evidence for the consumption of oxazine ring and allyl groups (Figure 3.12). The disappearance of the allylic =C–H, C=C stretching vibrations at 3075 and 1645 cm^{-1}, respectively, was clearly noted. There is obvious formation of hydroxyl peak belong

to phenolic of the polybenzoxazines at 3324 cm^{-1} and disappearance of the characteristic out-of-plane absorption modes of benzene with an attached oxazine ring are located at 924 cm^{-1} support the existence of ring-opened benzoxazines in the copolymer. Moreover, the stretching vibrations of aromatic C-H (3026–3065 cm^{-1}) and aromatic C=C (1452–1635 cm^{-1}), are detected. Hence, the incorporation of benzoxazines into polysulfide is confirmed since benzoxazines are the only aromatic compound involved in these reactions.

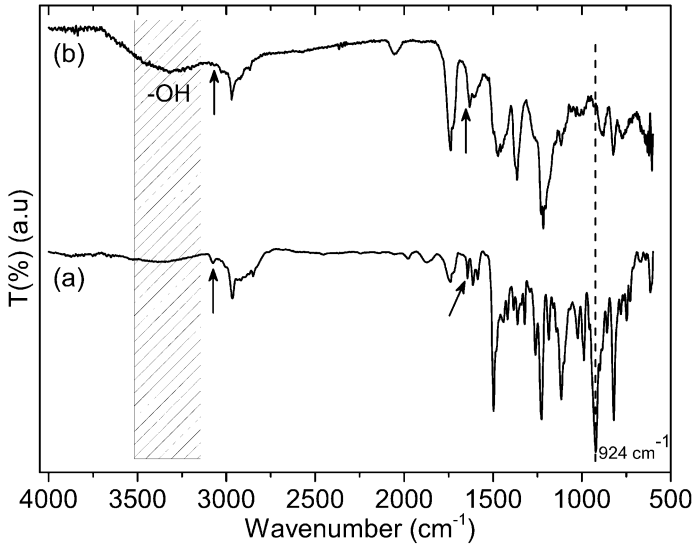


Figure 3.12 : FT-IR spectra of BA-ala (a), and poly(BA-ala-co-sulfur) with 50% S_8 (w/w) (b).

A crosslinked poly(benzoxazine-*co*-sulfur) was prepared using 80% BA-ala and 20% S_8 by weight to examine the surface properties of the network material. Upon drying the resin, an open, sponge-like network structure, probably originating from H_2S release, is obtained. SEM pictures of the material (Figure 3.13) reveal that there is no phase separation between polybenzoxazine and polysulfide structures, a complete mixing and smooth surfaces at micrometer level are visible. The observed bubble like structure is an additional evidence for the gas release.

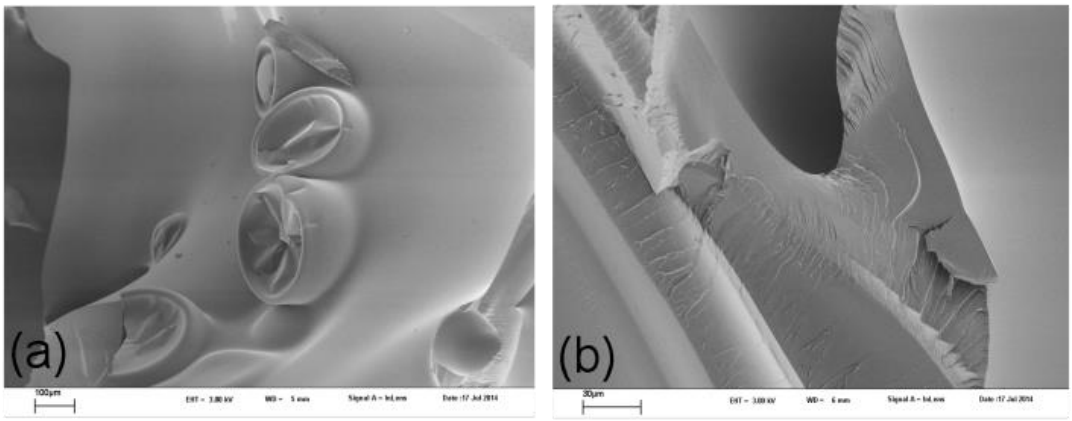


Figure 3.13 : SEM pictures of poly(BA-ala-*co*-sulfur) with feed ratio of 20%-wt S_8. The scales are 100 μm for (a) and 30 μm for (b).

It is known that depending on the functionalities present, the ring opening polymerization temperatures of benzoxazines generally lay between 150-260 °C. Figure 3.14 shows the DSC profile of BA-ala and an onset at 203 °C, end-set at 297 °C and the curing maximum at 266 °C are detectable for the ring-opening process.

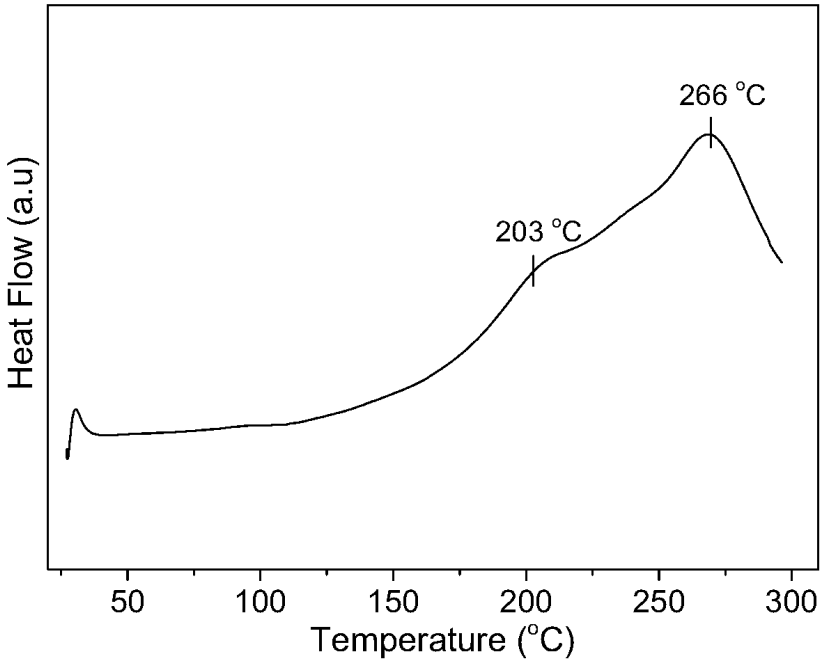


Figure 3.14 : DSC thermogram of BA-ala under N_2 nitrogen.

These values are affected by adding S_8 into BA-ala. As stated before the acidic conditions of the reaction decrease the onset ring-opening temperature of the oxazine ring down to 157 ˚C. The curing maximum of BA-ala and S_8 mixtures shifts to 182–184 ˚C with a *ca.* 82–84 ˚C reduction for all samples (Figure 3.15). The S_8 to BA-ala ratio has no real impact on ring–opening temperature of benzoxazine. In all the ratios studied on-set, end-set and maximum curing temperatures were close to each other as

tabulated in Table 3.2. Therefore, it can be deduced that the main effect on ring–opening temperature is H_2S formation during copolymerization reaction. However, the amount of added S_8 influences the amount of exotherm towards drop. This effect is certainly expected as S_8 itself does not participate in the curing process of oxazine, but takes part as an extra mass. Moreover, in each case, the melting endotherm of S_8 is easily detectable. This characteristic endotherm is used to track the traces of unreacted S_8 in the final copolymer. In Figure 3.16, melting endotherm of S_8 is detectable strongly for the samples with 90 and 80%-wt S_8. Besides, a slight endotherm is also visible for the sample containing 70%-wt S_8. These data reveals that the sulfur content of copolymers can only be slightly below 70% in such system. All the obtained copolymers are amorphous and thus, glass transition temperatures (T_g) are detectable from DSC. T_g values tend to shift to lower temperatures starting from 66 ˚C to 52 ˚C depending on the increasing sulfur content, consequently decreasing amount of polybenzoxazine hard segment in the copolymer. These data reveal that the copolymers start to degrade after *ca.* 210 ˚C, which is in accordance with thermogravimetric analysis (TGA) data (Figure 3.17).

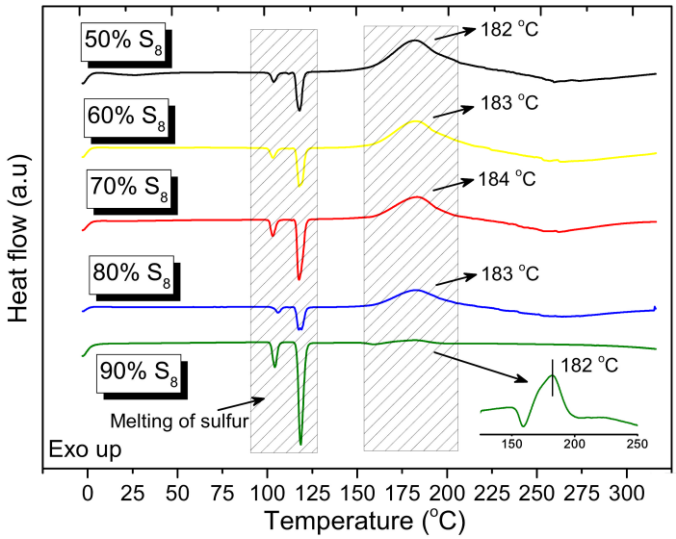


Figure 3.15 : DSC traces of BA-ala and S_8 reaction mixtures with varying S_8 content.

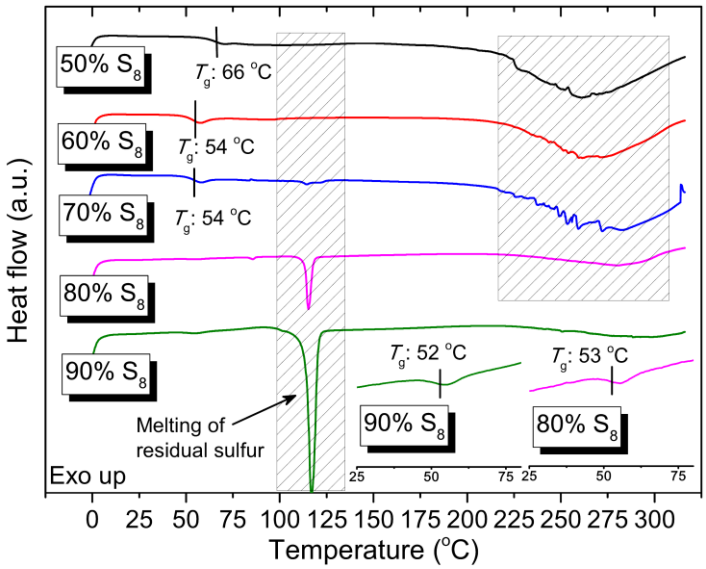


Figure 3.16 : DSC traces of poly(BA-ala-*co*-sulfur)s with varying S_8 content.

Table 3.2 : DSC[a] characteristics of BA-ala and its mixtures with various amounts of S_8.

Compound	On-set of Curing (°C)	End-set of Curing (°C)	Maximum Curing Temperature (°C)	Amount of Exotherm (J/g)
BA-ala[b]	203	297	266	-316
BA-ala + S_8 (50%)	157	205	182	-235
BA-ala + S_8 (60%)	158	201	183	-175
BA-ala + S_8 (70%)	159	203	184	-150
BA-ala + S_8 (80%)	160	208	183	-142
BA-ala + S_8 (90%)	161	195	182	-11

[a]DSC thermograms were collected under 20 mL.min^{-1} N_2 flow and 10 °C.min^{-1} heating rate.
[b]DSC thermogram of BA-ala is presented in supporting information.

Thermal stability of the BA-ala and related sulfur copolymers was explored by TGA under N_2 atmosphere. The TGA and derivative TGA curves of the cured BA-ala and its copolymers are shown in Figure 3.17 and 3.18. The related TGA results are collected in Table 3.3.

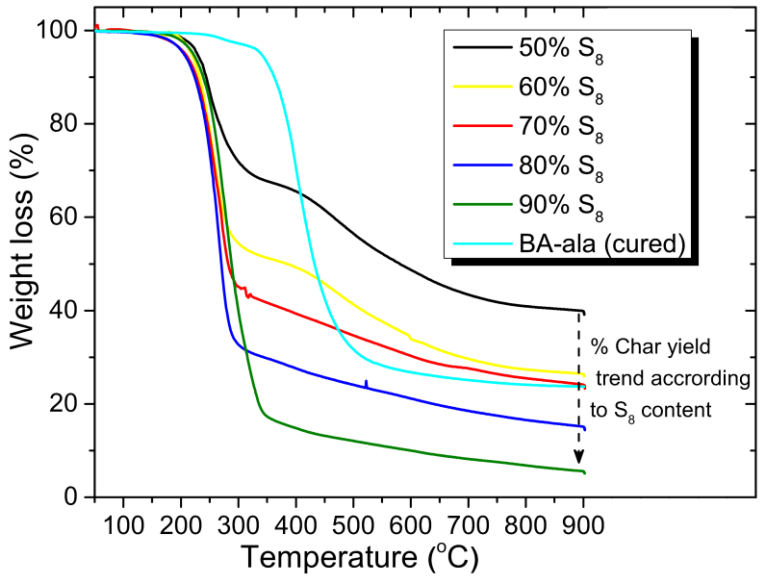


Figure 3.17 : TGA thermograms of BA-ala (cured) and poly(BA-ala-*co*-sulfur)s.

The degradation temperatures $T_{5\%}$, $T_{10\%}$ and T_{max} of poly(BA-ala-*co*-sulfur)s are lower than that of the corresponding BA-ala (cured) which can be possibly attributed to the relatively weak S–S bond in the bulk structure. Therefore, the apparent stability of polysulfide part regulates the overall thermal stability of the copolymers. However, the initial degradations temperatures of copolymers are higher than S_8 and pristine polysulfide due to the stamina of polybenzoxazine part in the copolymer. The pronounced effect of the sulfur groups is also detectable from the char yields of all the copolymers. Increasing sulfur content in the bulk system decreases the char yield at 800 ˚C. It should be noted that most of the char yield depression stem from unreacted sulfur domains in the copolymers having S_8 feed ratio more than 70%-wt. In contrast, bonded sulfurs have a positive effect on char yield compared to pristine BA-ala (cured). Moreover, it should be noted that there appears to be a change in the degradation of poly(BA-ala-*co*-sulfur) with 60% S_8. From the DSC data, there is no residual S_8 for this particular copolymer. The char yield drop in this case can be attributed to the dilution effect of S_8, which decreases the number collusions of BA-ala's, thus a critical point could be exceeded and smaller organic segments formed affecting the char yield.

Table 3.3 : Thermogravimetric properties of the BA-ala (cured) and related copolymers.

Polymer	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	T_{max} (°C)	Y_c (%)
BA-ala (cured)	342	362	397	24
Poly(BA-ala-*co*-sulfur) 90% S_8	219	283	275	6
Poly(BA-ala-*co*-sulfur) 80% S_8	206	222	265	17
Poly(BA-ala-*co*-sulfur) 70% S_8	207	227	261	26
Poly(BA-ala-*co*-sulfur) 60% S_8	218	232	256	28
Poly(BA-ala-*co*-sulfur) 50% S_8	227	243	246	41

$T_{5\%}$: The temperature for which the weight loss is 5%
$T_{10\%}$: The temperature for which the weight loss is 10%
T_{max}: The temperature for maximum weight loss.
Y_c: Char yields at 800 °C under nitrogen atmosphere

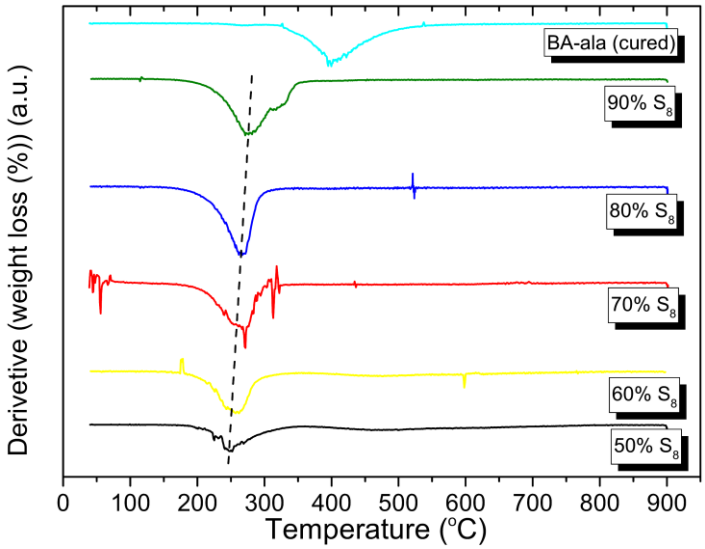


Figure 3.18 : Derivative weight loss (%) of BA-ala and related copolymers.

3.2 Experimental

3.2.1 Materials

4,4'-isopropylidenediphenol (bisphenol A) (Aldrich, 97%), paraformaldehyde (Acros, 96%), allylamine (Aldrich, 98%), sulfur (S_8, colloidal powder, reagent grade, Aldrich), sodium hydroxide (Acros, >97%), sodium sulfate (Acros, 99%), 1,4-dioxane (Aldrich, 99%), diethylether (Aldrich, ≥98%,), methanol (MeOH, Aldrich, 99%), Tetrahydrofuran (THF, VWR Chemicals, 99.7%), Chloroform-d (CDCl3, 99.8 atom % D) were used as received.

3.2.2 Characterization

All ^{1}H NMR spectra were recorded on an Agilent NMR System VNMRS 500 spectrometer at room temperature in $CDCl_3$ with $Si(CH_3)_4$ as an internal standard. FT-IR spectra were recorded on a Perkin-Elmer FT-IR Spectrum One spectrometer. Differential Scanning Calorimetry was performed on Perkin–Elmer Diamond DSC from 30 ˚C to 320 ˚C with a heating rate of 10 ˚C min. under nitrogen flow (20 $mL.min^{-1}$). A typical DSC sample was 2–5 mg in a 30 μL aluminum pan. Thermal gravimetric analysis (TGA) was performed on Perkin–Elmer Diamond TA/TGA with a heating rate of 10 ˚C min under nitrogen flow. A typical TGA sample was 5–10 mg in a platinum pan. Gel permeation chromatography (GPC) measurements were performed on a Viscotek GPC max auto sampler system consisting of a pump, light-scattering detector (λ= 670 nm, Model 270 dual detector, Viscotek Corp.) consisting of two scattering angles: 7˚ and 90˚ and Viscotek a differential refractive index (RI) detector with three ViscoGEL GPC columns (G2000H HR, G3000H HR, and G4000H HR, 7.8 mm internal diameter, 300 mm length) in series. The effective molecular weight ranges were 456−42 800, 1050−107 000, and 10 200−2 890 000, respectively. THF was used as an eluent at flow rate of 1.0 mL min^{-1} at 30 ˚C. Both detectors were calibrated with PS standards having narrow-molecular-weight distribution. Data were analyzed using ViscotekOmniSEC Omni-01 software.

3.2.3 Synthesis of 6,6′-(propane-2,2-diyl)bis(3-allyl-3,4-dihydro-2H-benzo[e][1,3] oxazine) (BA-ala)

In a 250 mL round bottomed flask, allyamine (15.4 g, 0.270 mol) was dissolved in 1,4-dioxane (100 mL) and solution was cooled in an ice bath. Paraformaldehyde (16.2 g, 0.540 mol) was added portion-wise to this solution during 10 min. Then, bisphenol-A (30.8 g, 0.135 mol) was added to the solution and the mixture was refluxed for 24 h. The solvent was evaporated using a rotary evaporator. The resulting oily product was dissolved in diethyl ether (150 mL) and extracted with 0.1 N sodium hydroxide for various times to remove unreacted bisphenol A. Then, to neutralize the solution diethyl ether solution washed with distilled water (50 mL) for two times. The solution was dried with anhydrous Na_2SO_4 and filtered. Diethyl ether was evaporated under vacuum and remaining oily product was dissolved in MeOH (15 mL). Water was added drop by drop into MeOH solution until it became turbid, and then refrigerated (4°C). The precipitated sticky mass was obtained by

decantation of MeOH and washing with excess water. The product was dried under vacuum at 60 °C for 24 h. (Yield, 65%).

3.2.4 General procedure for the preparation of poly(benzoxazine-*co*-sulfur)

To a 20 mL test tube, equipped with a magnetic stir bar, sulfur and allylbenzoxazine was added. The tube was heated up to 185 ˚C with vigorous stirring in an oil bath. In the first 2 minutes a clear orange solution is formed and became transparent yellow subsequently. Then, the color of the solution changed to brown-black after 10 min. The overall reaction time was 30 min. in total. After cooling the tube to r.t. it was broken and the product was collected. In these reactions, sulfur feed ratios was 50, 60, 70, 80 and 90-wt%.

3.3 Conclusion

In conclusion, we have demonstrated that elemental sulfur and allyl functional benzoxazines can thermally react to form network structured and soluble copolymers. At low S_8 feed ratios only soluble copolymers are obtained. The synthetic methodology described here is relatively easy and fast, which can be achieved in 30 min. by a simple melt process. This process can be called as inverse vulcanization of benzoxazines. The curing of benzoxazine and inverse vulcanization take place simultaneously and/or sequentially producing copolymer with high sulfur content. Of course, the critical issue for this process is to use suitable benzoxazines with allyl functionality. In this context, the design flexibility of benzoxazine chemistry provides a vast number of different possible allyl functional benzoxazines giving opportunity to use this approach efficiently. Moreover, the gas release during the synthesis can be profited to fabricate sponge like polybenzoxazine materials when the feed ratio of S_8 decreased for example 20%-wt. Another important advantage is the reduction of the ring-opening temperature of benzoxazine about 84 ˚C due to the acidic medium. The most appealing part of this strategy is its simplicity and low cost of the chemicals can be converted into advanced materials using the conditions outlined here in one-pot.

4. POST MODIFICATION OF POLYBUTADIENES BY PHOTOINDUCED HYDROGEN ABSTRACTION FROM BENZOXAZINES AND THEIR THERMALLY ACTIVATED CURING[3]

Polybutadiene (PB) has been produced in large volumes as synthetic rubber in the world. It has found many applications, particularly in the production of treads and sidewalls in tires. Another major application is the high impact resin modification. In most of these application, it is used in the copolymer form as acrylonitrile-butadiene-styrene resin (ABS). Some other less customary but interesting applications of PBs, including composites, soft films, adhesives, and coatings are also available. It appears that PB will continue to be an important material for various applications due to its low cost, availability and unique properties. Thus, increased demand would lead to develop new PBs with higher performance [121-123].

Raw PBs generally exhibit weak thermal properties and generally has char yields below 3−5% at 800 °C. The crosslinking enabled reinforcement of rubbers enhances mechanical properties along with thermal properties. The cross-linking of rubbers can be realized by peroxide curing or more generally by sulfur vulcanization [124-126]. However, for some applications the conventional systems may be inappropriate and new crosslinking processes through incorporation of appropriate functional groups on PBs are required. Among various alternative cross-linking methods photocuring conducted under relatively mild conditions appeared to be one of the most suitable approach to achieve desired network formation. Styrene− butadiene rubber, having approximately 8% pendant vinyl double bonds (1,2-residue), was converted to the insoluble network upon UV irradiation at ambient conditions. Similarly, addition of diacrylate monomers, which copolymerizes with the 1,2- and 1,4- double bonds, yielded networks with enhanced efficiency. In an alternative approach, multifunctional thiols were used to photochemically cross-link PBs at ambient temperature via thiol−ene reaction [127-129]. Resole or novolac type

[3] This chapter is based on the paper, **Arslan M.,** Kiskan B., and Yagci Y., Post-Modification of Polybutadienes by Photoinduced Hydrogen Abstraction from Benzoxazines and Their Thermally Activated Curing. *Macromolecules*, 49, 14, 5026-5032.

phenolics, extensively used with various polymers, were reported to be another common method in PB crosslinking providing significant decrease of inherent brittleness of phenolics and improvement of toughness [130]. Recently, polybenzoxazines as a class of polyphenolic thermosets formed by ring-opening polymerization of the 1,3-benzoxazines without using any catalyst (Figure 4.1) progressively substitute resole or novalac type phenolics [9, 15, 16]. These thermosetting materials attract a great interest in diverse scientific and industrial areas due to their superior properties such as high char yield and flame resistance, low water intake, high modulus and strength, high glass transition temperatures, dimensional stability upon curing, chemical resistance, and long shelf life for their monomers. The synthesis of benzoxazine monomers is relatively easy and requires a primary amine, a phenol derivative, and formaldehyde (Figure 4.1) [7, 15, 31, 43, 74, 131].

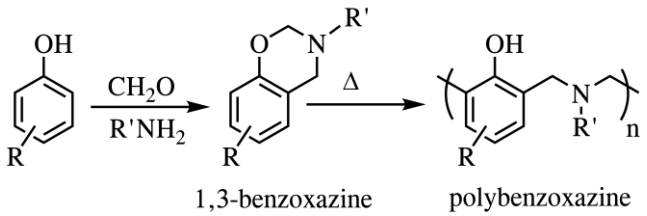


Figure 4.1 : Synthesis of 1,3-benzoxazine monomer and its polymerization.

Such synthetic simplicity creates a high capacity for various molecular designs. Despite the obvious advantages, most of the polybenzoxazines exhibit brittleness, although this is not necessarily an inherent property of polybenzoxazines. Generally, three main approaches are used both to overcome this problem and also improve the existing properties of polybenzoxazines: (1) synthesizing target based novel monomers [13, 26, 132-134], (2) blending with various polymers or fibers and fillers, [16, 39, 46, 135-137], or (3) synthesizing polymers containing benzoxazines as side-chain, end-chain, or main-chain [14, 18, 32, 36, 37, 138-144]. In this context, the essential brittleness of the thermosets can successfully be reduced by the modification with rubber. The addition of reactive rubber for toughening polybenzoxazines without sacrificing existing properties has also been demonstrated. Also, liquid rubber and difunctional benzoxazine mixtures afforded tough materials after curing [145-147]. However, blending method has problems associated with nonuniform distribution of rubber in benzoxazines, which generally reduces the mechanical strength of the material. In a previous study, we have incorporated

benzoxazines onto PB backbone by using click chemistry to circumvent this problem. It should, however, be noted that this method requires successive bromination and azidation of PB [80]. Instead, photochemistry in conjunction with benzoxazine chemistry has capacity to modify PBs or similar polymers in one step. Such an approach has various advantages because it is well-known that photoinitiated systems are rapid even at law temperatures, meet environmental issues, and consume low energy. These advantages are important in several industrial practices including adhesives, coatings, printing inks, photoresists and more [148]. Photoinitiator systems that initiate free radicals by a bimolecular process were studied extensively. In these systems, initiation goes through with formation of a triplet excited state of an aromatic carbonyl and then hydrogen abstraction from a donor molecule (co-initiator). Mostly, polymerization of vinyl monomers is started by the radicals generated on the hydrogen donor. On the contrary, the ketyl radicals are usually nonreactive against vinyl monomers due to delocalization of unpaired electron and the steric hindrance [149-151]. Typical photoinitiators of this type are thioxanthones, benzophenones, benzil and quionones while amines, thiols, alcohols, and ethers serve as hydrogen donors [152, 153]. Thus, such a photoinitiator does not require a separate molecular hydrogen donor acting as additional co-initiator. As part of our ongoing research interest for developing new photochemical systems for macromolecular synthesis, we now report the use of benzoxazine as both hydrogen donor and aromatic carbonyl photosensitizer to incorporate benzoxazines onto a PB backbone in one simple step.

4.1 Results and Discussions

Photosensitizers that have both hydrogen donor and aromatic carbonyl do not require an additional co-initiator as stated in the introduction. For this purpose, 4-hydroxybenzophenone (4-HBPh) and vanillin (Van) was reacted with primary aromatic amines (*p*-toluidine for 4-HBPh and aniline for Van) and formaldehyde to obtain benzophenone and vanillin based benzoxazines (BPh-ptol and Van-a), respectively (Figure 4.2).

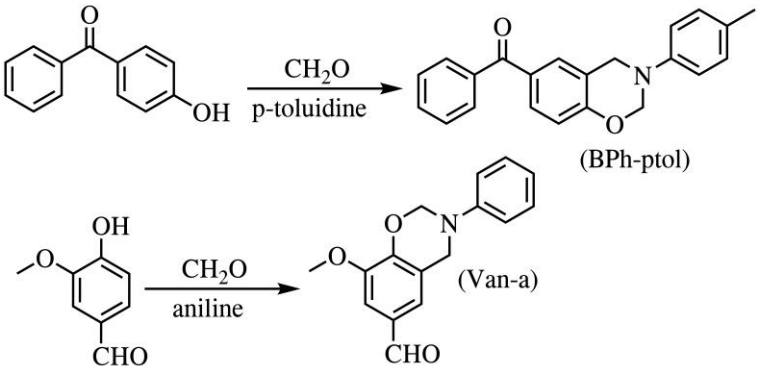


Figure 4.2 : Synthesis of benzophenone-benzoxazine (BPh-ptol) and vanillin-benzoxazine (Van-a).

The chemical structure of the BPh-ptol and Van-a was confirmed by spectral analysis. As shown in Figures 4.3 and 4.4, the ^{1}H NMR spectra of the monomers display the specific signals of benzoxazine ring. Particularly, the two NMR peaks in the range of 5.43 and 4.66 ppm for BPh-ptol, 5.51 and 4.68 for Van-a corresponding to −CH2 protons of benzoxazine rings are revealed. Moreover, in Figure 4.4 the aldehyde proton of Van-a is clearly visible at 9.78 ppm.

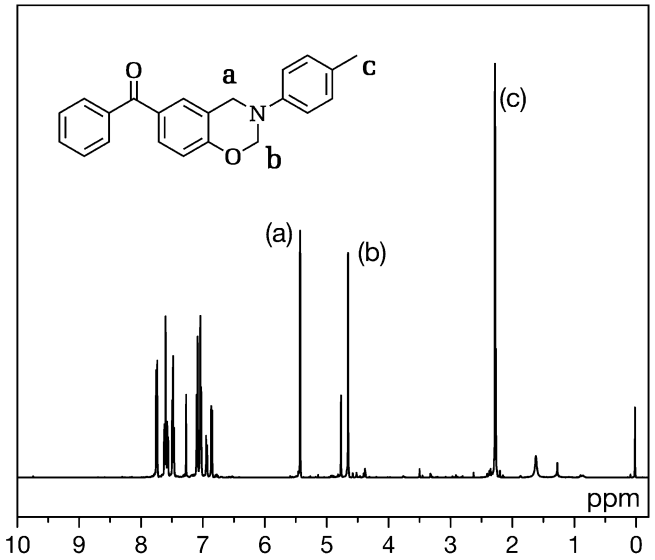


Figure 4.3 : ^{1}H NMR spectrum of BPh-ptol.

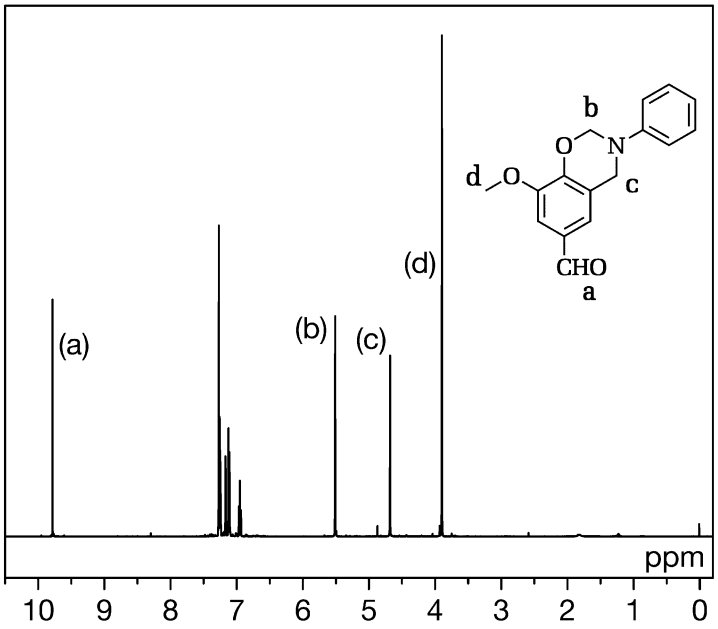


Figure 4.4 : ^{1}H NMR spectrum of Van-a.

The FT-IR transmittance bands of the benzoxazines were reported previously in detail [154, 155]. Accordingly, in Figure 4.5 and 4.6, the characteristic bands of IR absorptions of benzoxazines emerged at 928 and 1495 cm^{-1} for BPh-ptol, 917 and 1493 cm^{-1} for Van-a can be assigned to the trisubstituted benzene ring. The peak at 1232 cm^{-1} is attributed to the C−O−C asymmetric stretching vibration of benzoxazine rings. A more detailed view of the region below 1700 cm^{-1} of Figure 4.5 and 4.6 is included in the supporting information as Figure 4.7.

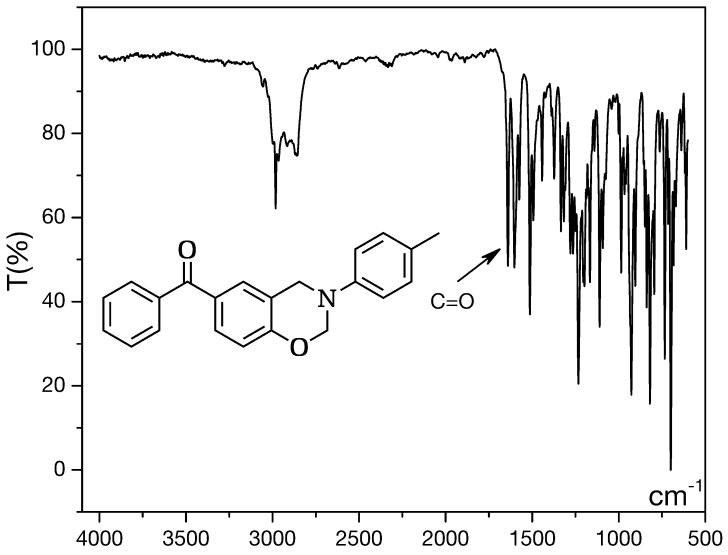


Figure 4.5 : FT-IR spectrum of BPh-ptol.

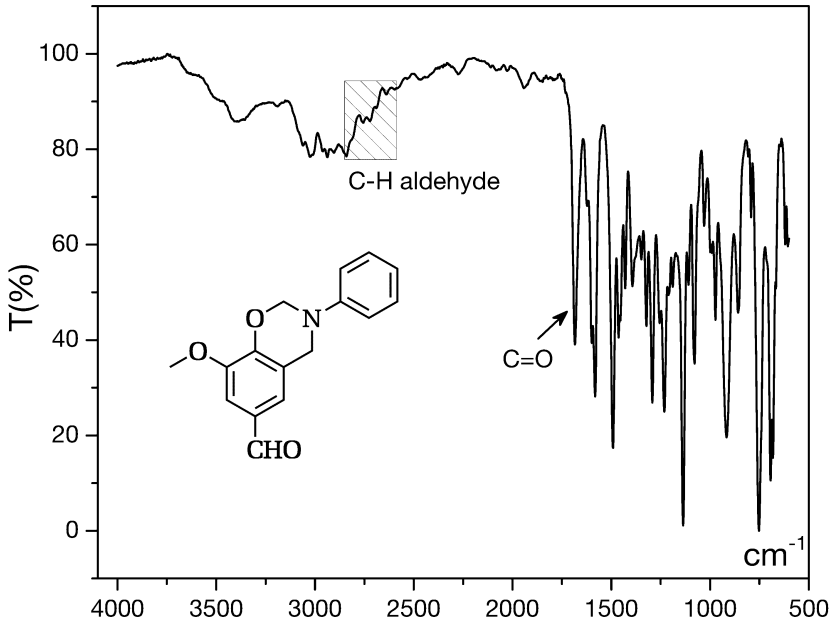


Figure 4.6 : FT-IR spectrum of Van-a.

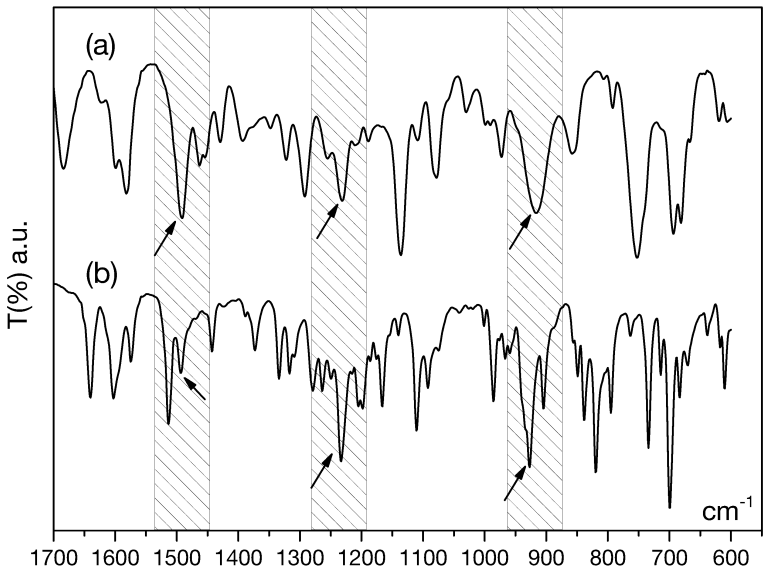


Figure 4.7 : Overlaid FT-IR spectra for region below 1700 cm^{-1} of Van-a (a) and BPh-ptol (b).

^{13}C NMR spectra of both monomers also confirm their structures. In Figure 4.8 and 4.9, the oxazine ring carbons are clearly detectable at 80.6 (N–**C**H_2–O) and 50.7 (Ar–**C**H_2–O) ppms, moreover carbonyl carbon emerges at 195.5 ppm.

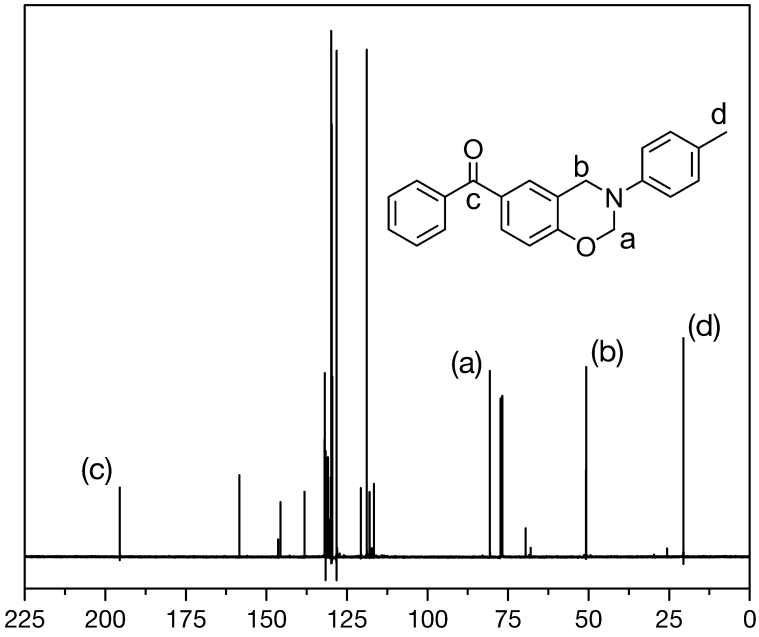


Figure 4.8 : ^{13}C NMR spectrum of BPh-ptol.

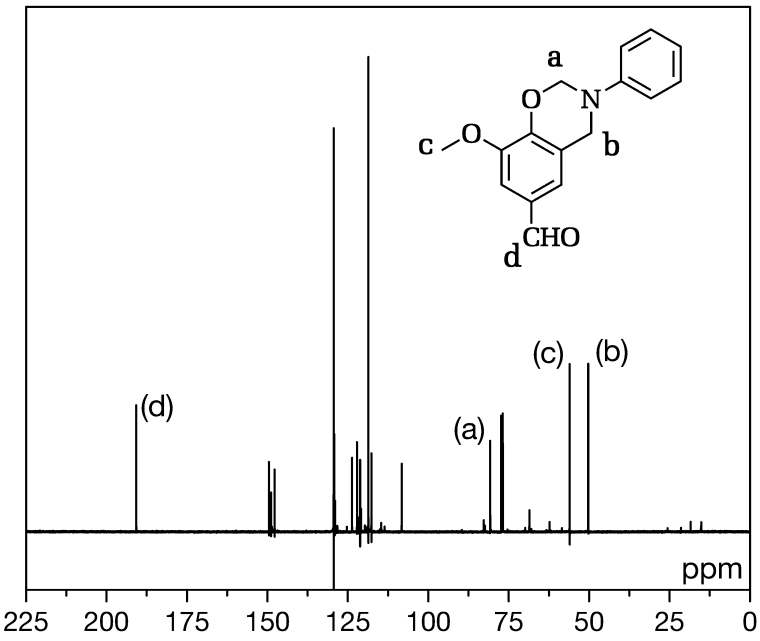


Figure 4.9 : ^{13}C NMR spectrum of Van-a.

The photoinduced hydrogen abstraction reactions of aromatic carbonyls with amines are highly dependent on the absorption characteristics, intersystem crossing efficiency and structures of the amines used. In particular, hydroxyalkyl substituted tertiary amines were introduced to be efficient hydrogen donors. Also, dialkyl anilines were used in those photo systems with success depending on the substituents. In this perspective, the oxazine ring contains an inner dimethyl aniline group on its structure that is suitable for hydrogen donation.

The usage of benzoxazines in photoinitiated free radical polymerization of acrylates in aforementioned manner was previously reported by our group. In the reported study, the hydrogen abstraction reactions of various photoexcited aromatic carbonyl compounds, namely benzophenone, thioxanthone, 2-chloro-thioxanthone, 2-isopropyl-thioxanthone and camphorquinone with a mono-functional benzoxazine (P-a: benzoxazine derived from aniline and phenol) were shown[3]. Interestingly, P-a exhibited initiation efficiency almost the same as co-initiator trimethylamine under similar experimental conditions in the photopolymerizations [156].

In the present work, the initiating action of BPh-ptol and Van-a are based on bimolecular process containing electron transfer with a subsequent hydrogen abstraction, resulting in the generation of benzoxazine radical according to the following reactions (Figure 4.10). Because of the rigidity of the structures the benzoxazine compounds, the radicals are expected to be formed from intermolecular hydrogen abstraction process.

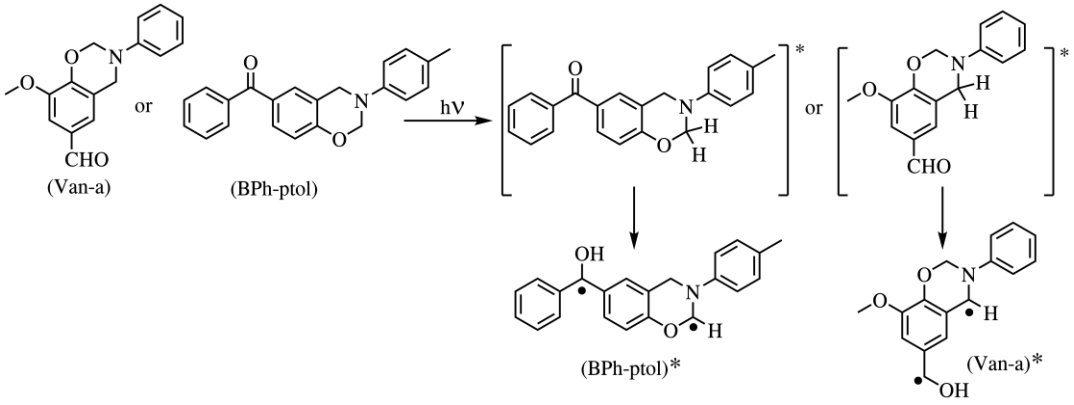


Figure 4.10 : Light induced radical formation on BPh-ptol and Van-a monomers.

The proposed mechanism involving hydrogen abstraction from benzoxazines was readily obtained by spectral analysis previously elsewhere [157]. As shown in Figure 4.10, in the modification process all the emitted light is absorbed by the benzoxazine compounds as PB is transparent at the irradiation wavelength. Thus, the covalent binding of benzoxazine molecules onto PB by the defined photoinitiating route (Figure 4.12) was realized without any interfering component.

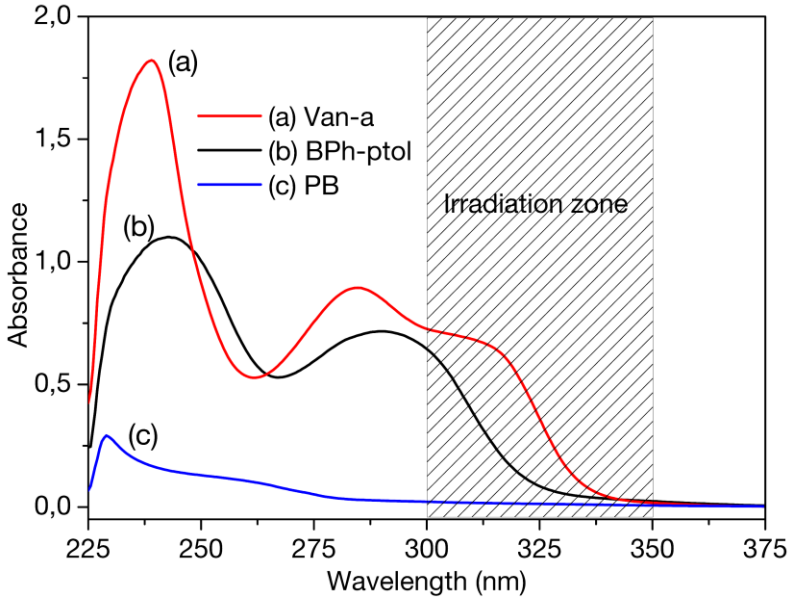


Figure 4.11 : UV-Vis spectra of Van-a (a), BPh-ptol (b), PB (c). The monomer concentrations are 6.25×10^{-5} M ($CHCl_3$).

The reaction was performed simply by mixing PB with BPh-ptol or Van-a in chloroform ($CHCl_3$) in a pyrex tube and irradiated in a photo reactor for a certain time. After precipitation of modified PB in hexane and washing to remove un-reacted benzoxazine monomers, poly(butadiene-*co*-BPh-ptol) or poly(butadiene-*co*-Van-a) was obtained. The increment of the number average molecular weight (M_n) of PB from 6300 to 7660 Da, obtained by GPC measurements, is an evidence for the covalent attachment of benzoxazines to the polyolefin structure. In the absence of the benzoxazine compounds, control experiment involving irradiation of PB in $CHCl_3$ failed to result in a significant molecular weight increase discarding the possibility of direct photoinduced radical generation from PB and coupling processes.

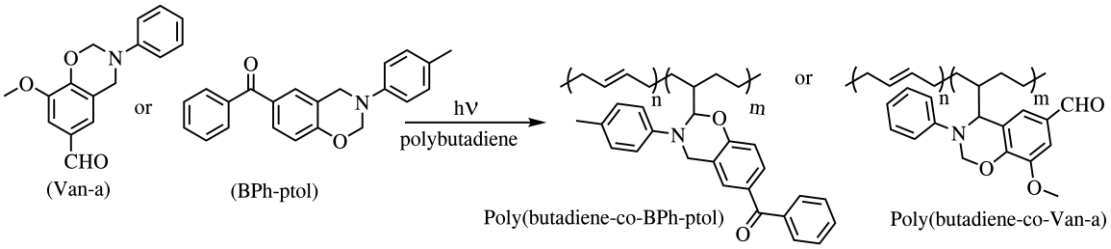


Figure 4.12 : Light induced post modification of polybutadiens by BPh-ptol and Van-a.

As shown in Figure 4.14, the spectra of the corresponding modified PBs present not only the specific signals of PB, but also chemical shifts belonging to the benzoxazine moiety. Notably, the protons at around 4.6 ppm ($N-CH_2-Ph$) shift to 3.77 for BPh-ptol and 4.07 for Van-a while the protons at 5.43 and 5.51 ppm ($N-CH_2-O$) remains

at the same position after hydrogen abstraction and addition reactions. However, those signals overlap with double bond protons of PB that cover the range of 5.20−5.52 ppm. These results indicate that hydrogen abstraction takes place dominantly at N−CH_2−Ph carbon atom. This can be anticipated because hydrogen abstraction from benzylic carbon would lead to the formation of more stable radicals. A more detailed spectral analysis was performed using ^{13}C NMR technique and the N−CH_2−O carbon for oxazine rings was clearly detected at 80.7 ppm after incorporation of benzoxazines into PB. Moreover, as observed in ^{1}H NMR spectra of modified PBs, a shift was also seen for N−CH 2−Ph carbon of both oxazines from 50.7 to 55.2 ppm, further supporting the point that the emphasized hydrogen abstraction is mainly occurring at N−CH_2−Ph carbon (see Figure 4.13).

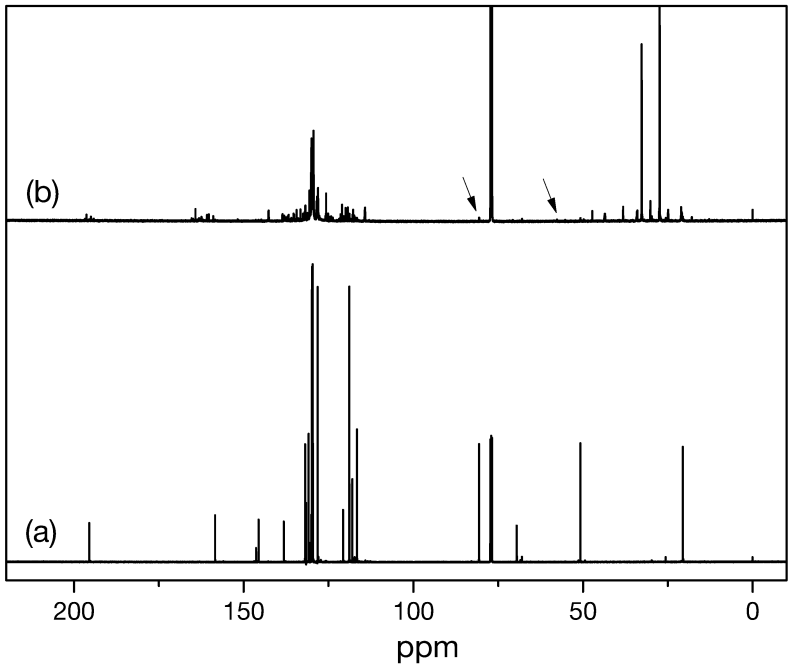


Figure 4.13 : ^{13}C NMR spectra of BPh-ptol (a), and poly(butadiene-*co*-BPh-ptol).

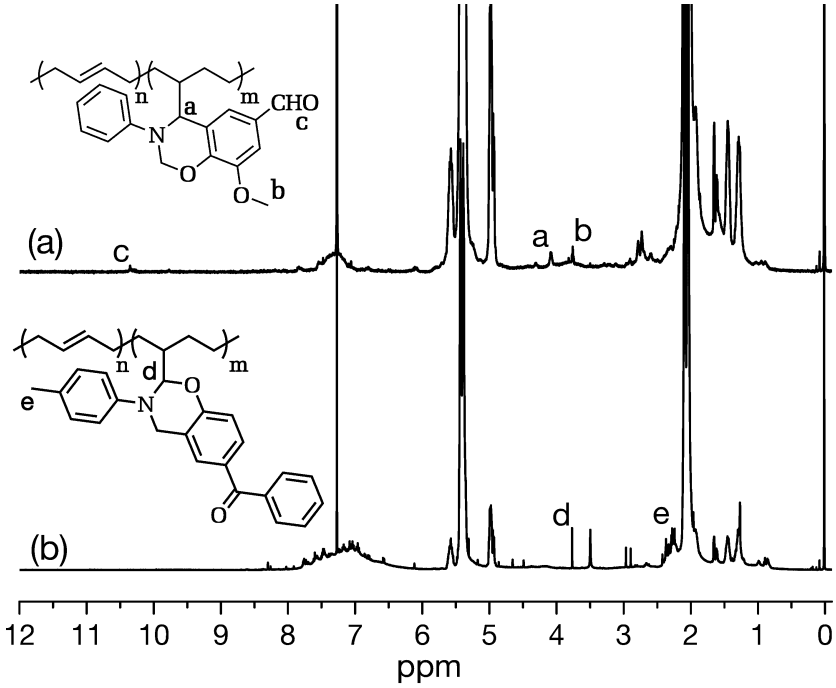


Figure 4.14 : Overlaid ^{1}H NMR spectra of poly(butadiene-*co*-Van-a) (a), and poly(butadiene-*co*-BPh-ptol) (b).

The covalent binding of benzoxazines onto PB by means of the reported photoinitiating system especially is useful for cross-linking of thick films. Thus, we have performed DSC studies to present curing characteristics of poly(butadiene-*co*-BPh-ptol) and poly(butadiene-*co*-Van-a). As known, benzoxazines can be polymerized via ring-opening reaction when heated up to certain temperatures and these ring-opening polymerization temperatures generally lie between 150 and 260 °C depending on the substituents on the benzoxazines. The concentration and/or mobility of benzoxazine molecules in a medium determines the possibility of self-collisions which have high impact on the ring-opening temperature and exotherm apart from structure of any benzoxazine. This effect can be observed clearly when identical benzoxazine monomers are compared with different concentrations, and the diluted samples would have a higher ring-opening temperature. Consequently, any kind of dilution or reduction in mobility would be effective on curing behavior. This phenomenon can be also seen for polymers with benzoxazines end-chains. In the case of molecular weight increments for such polymers could increase the curing temperature even up to 300 °C. According to GPC results each PB chains were modified by 4−5 benzoxazines after irradiation. Thus, a small amount of dilution effect is observed for poly(butadiene-co-BPh-ptol) and poly- (butadiene-co-Van-a) in DSC analysis. In both Figure 3 and 4, a small and shifted ring-opening exotherms

can be detected at 238 °C for poly(butadiene-co-BPh-ptol) and 234 °C for poly(butadiene-co-Van-a). The collected data for monomers and modified PBs is tabulated in Table 4.1.

Table 4.1 : DSC[a] Characteristics of Van-a, BPh-ptol, poly(butadiene-*co*-BPh-ptol), poly(butadiene-*co*-Van-a).

Monomer/ Polymer	**On-set of Curing (°C)**	**End-set of Curing (°C)**	**Maximum Curing Temperature (°C)**	**Amount of Exotherm (J/g)**
BPh-ptol[b]	174	248	208	-147
Van-a[c]	188	247	222	-138
Poly(butadiene-*co*-BPh-ptol)	224	245	234	-26
Poly(butadiene-*co*-Van-a)	232	246	238	-31

[a]DSC thermographs were collected under 20 mL.min^{-1} N_2 flow and 10 °C.min^{-1} heating rate.

[b,c]Detailed DSC thermographs can be found as figure 4.17 and 4.18.

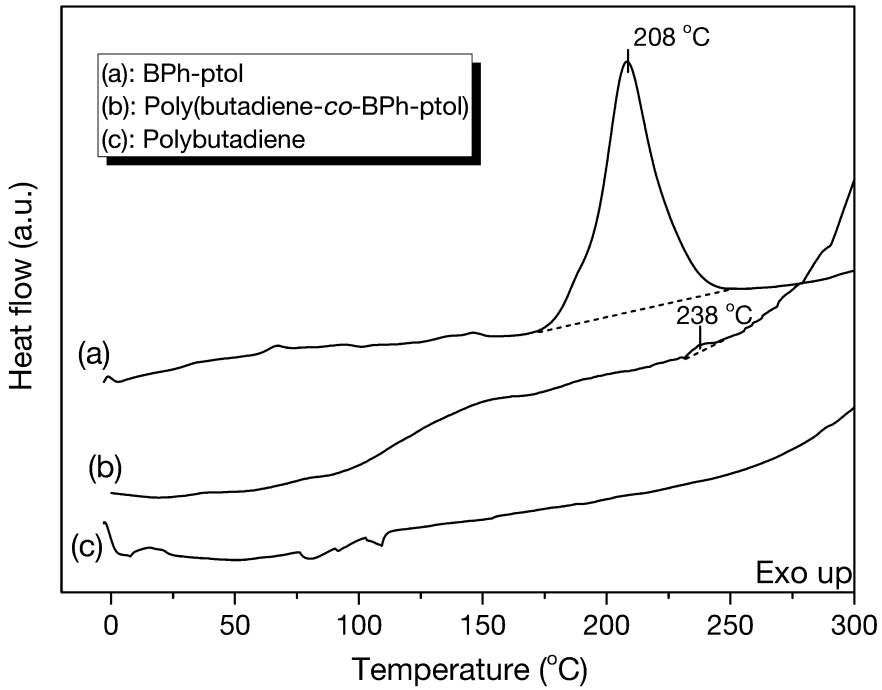


Figure 4.15 : DSC thermographs of BPh-ptol (a), poly(butadiene-*co*-BPh-ptol) (b), and light exposed polybutadiene (c).

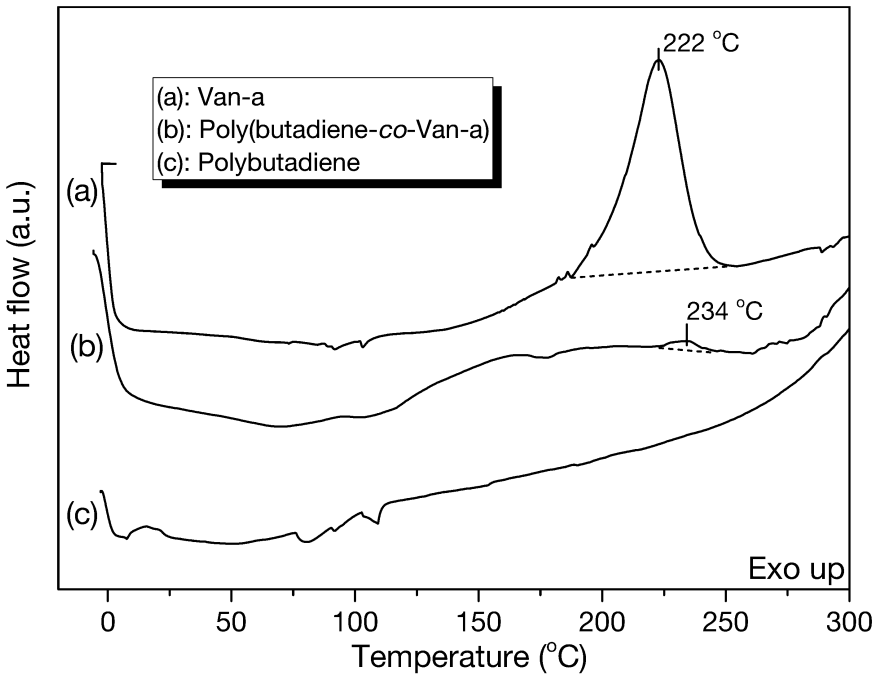


Figure 4.16 : DSC thermographs of Van-a (a), poly(butadiene-*co*-Van-a) (b), and light exposed polybutadiene (c).

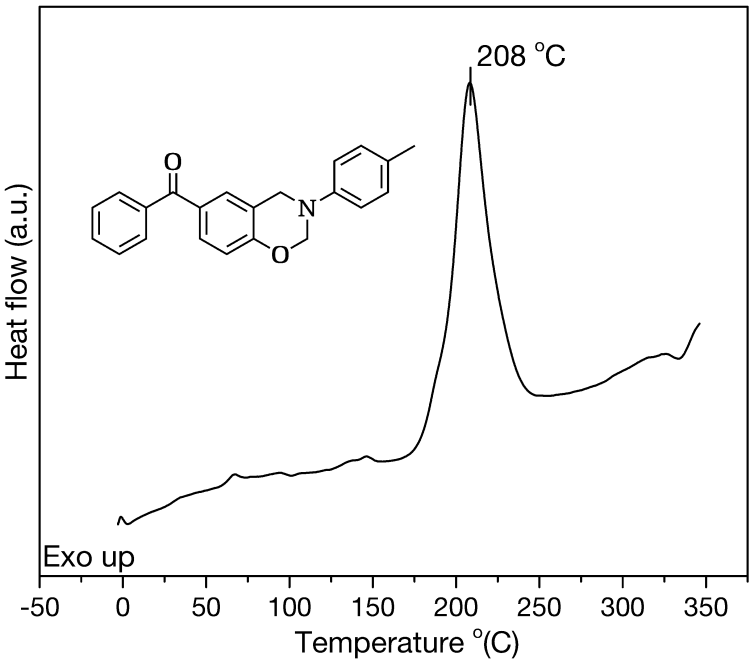


Figure 4.17 : DSC thermograph of BPh-ptol monomer.

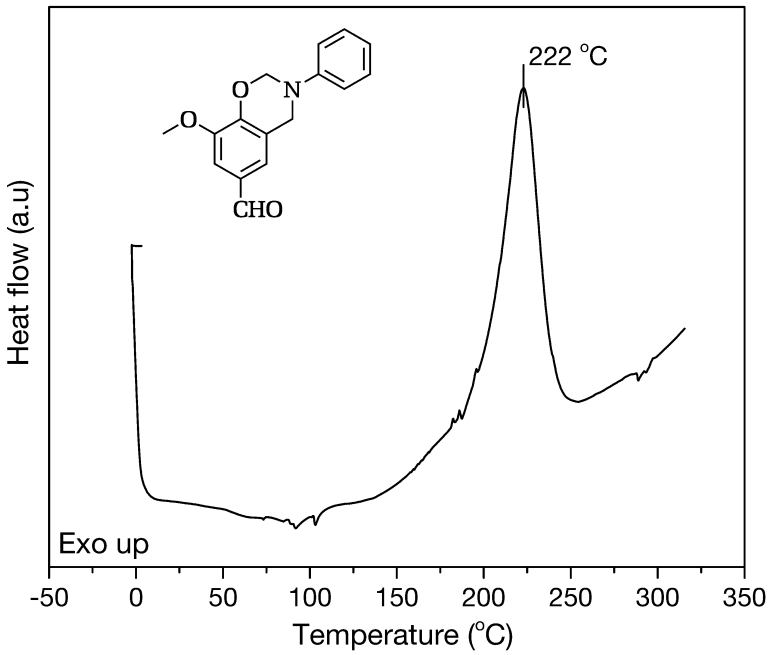


Figure 4.18 : DSC thermograph of Van-a monomer.

After curing, extraction of cured poly(butadiene-co-BPh-ptol) and poly(butadiene-co-Van-a) with tetrahydrofuran, which dissolves PB, did not remove significant amount of polymer from the resulting product indicating efficient curing process. However, the number of benzoxazines on each PB chain seems not sufficient for self-standing film. Hence, another additional monomer, namely Ba-ala, was mixed with poly(butadiene-coBPh-ptol) or poly(butadiene-co-Van-a) to prepare cured film. The visual image of this film is presented in Figure 4.19.

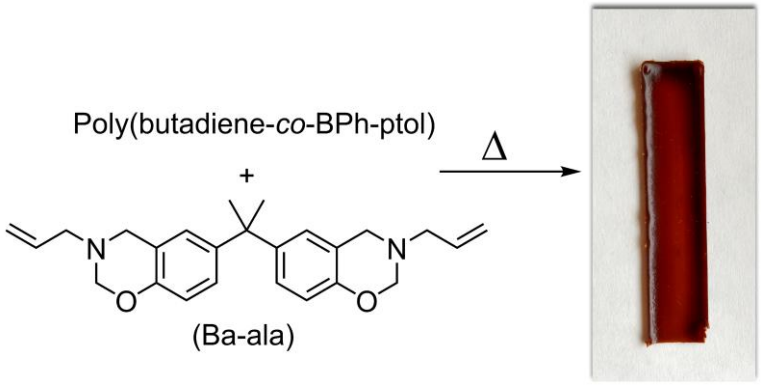


Figure 4.19 : Image of cured film of poly(butadiene-*co*-BPh-ptol) and allyl benzoxazine (Ba-ala).

Thermal endurance of the modified and cured PB polymers was analyzed by Thermal gravimetric analysis (TGA) in N_2 environment. The TGA thermographs of cured poly-(butadiene-co-BPh-ptol), poly(butadiene-co-Van-a), and unmodified PB

are depicted in Figure 4.20 and the thermal data are tabulated in Table 4.2. All the cured modified PB polymers apparently showed higher char yields compared to raw PB since benzoxazines established a network of PB polymers. Accordingly, pristine PB has left only 3% char at 800 °C and has almost completely vaporized after 800 °C.

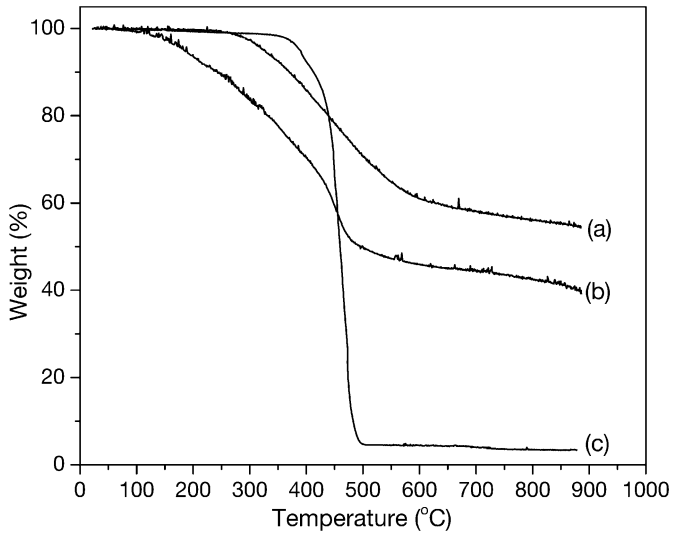


Figure 4.20 : TGA curves of cured poly(butadiene-*co*-Van-a) (a), poly(butadiene-*co*-BPh-ptol) (b) and pristine PB (c).

Table 4.2 : Thermogravimetric properties of the cured poly(butadiene-*co*-Van-a), poly(butadiene-*co*-BPh-ptol) and pristine PB.

Polymer	**$T_{5\%}$ (°C)**	**$T_{10\%}$ (°C)**	**T_{max} (°C)**	**Y_c (%)**
pristine PB	388	409	456	3
poly(butadiene-*co*-Van-a)	324	366	450	55
poly(butadiene-*co*-BPh-ptol)	183	239	433	42

$T_{5\%}$: The temperature for which the weight loss is 5%

$T_{10\%}$: The temperature for which the weight loss is 10%

T_{max}: The temperature for maximum weight loss.

Y_C: Char yields at 800 °C under nitrogen atmosphere

Poly(butadiene-*co*-Van-a) and poly(butadiene-*co*-BPh-ptol) exhibited char yields as 55% and 42%, respectively. The relatively higher chair yield with the vanilline based polymer most probably due to the higher amount of benzoxazine unit per PB chain. It is clear that the incorporation of benzoxazines into PB drastically increased the char yield. The same effect was also observed for polyvinylchloride and polystyrene modified with benzoxazine. Conversely, initial degradations of poly(butadiene-*co*-

Van-a) and poly(butadiene-*co*-BPh-ptol) occur at lower temperatures at $T_{5\%,}$ and $T_{10\%}$ probably due to the decarbonylation reactions [158].

4.2 Experimental

4.2.1 Materials

4-Hydroxybenzophenone (Alfa Aesar), paraformaldehyde (Acros, 96%), *p*-toluidine (Merck), ethanol (≥99.5%, Aldrich), hexane (Aldrich, 95%), toluene (Carlo Erba, 99.5%), allyl amine (Aldrich, 98%), chloroform (Acros, 99+%), vanillin (Alfa Aesar, 99%), aniline (Merck, 99%), dichloromethane (99.8%, Baker), 4,4′-isopropylidenediphenol (Aldrich, 97%), 1,4-dioxane (Aldrich, 99%), sodium hydroxide (Acros, > 97%), methanol (MeOH, Aldrich, 99%), diethyl ether (Carlo Erba, 99.8%), sodium sulfate (Acros 99%), and polybutadiene (M_n = 6300, Elastomeros Processing Co.) were used as received.

4.2.2 Characterization

^{1}H NMR spectra were obtained by using an Agilent NMR System VNMRS 500 spectrometer at ambient temperature. All the deuterated NMR solvents contained $Si(CH_3)_4$ as internal standard. Perkin−Elmer FT−IR Spectrum One spectrometer was used for IR analysis that equipped with Pike Miracle Accessory (ZnSe) for attenuated total reflection (ATR) and cadmium telluride detector. A total of 24 scans were performed for each spectrum and resolution was set to 4 cm^{-1}. Perkin−Elmer Diamond TA/TGA device was used for thermal gravimetric analysis (TGA). All the measurements were performed under nitrogen and 10 °C/min heating rate was used. Thermal behaviors of materials were analyzed by using a Perkin−Elmer Diamond DSC device. All of the differential scanning calorimetry (DSC) experiments were carried out under 20 mL/min nitrogen flow, and a 10 °C/min heating rate was used. Gel permeation chromatography (GPC) analyses were performed using a Viscotek GPC max with a Viscotek UV detector and a Viscotek differential refractive index (RI) detector. The GPC columns were ViscoGEL (G2000H HR, G3000H HR, and G4000H HR, 300 mm length, 7.8 mm internal diameter) and THF was used as an eluent at flow rate of 1.0 mL/min. Analyses were performed against PS standards. Data were collected by ViscotekOmniSEC Omni-01 software.

4.2.3 Synthesis of benzophenone benzoxazine (BPh-ptol)

In a 250 mL round bottomed flask were dissolved 4-methylphenol (*p*-toluidine) (10.1 mmol, 1.08 g), paraformaldehyde (20.2 mmol, 0.61 g), and 4-hydroxybenzophenone (10.1 mmol, 2 g) in 30 mL of toluene and 15 mL of methanol mixture. The content was refluxed for 24 h. The solvent was evaporated under vacuum. The chloroform solution of the product was successively washed three times with 0.1 M NaOH solution and deionized water. Chloroform layer was dried with anhydrous Na_2SO_4, filtered and then solvent was removed under vacuum. Finally, the product was dried at ambient temperature in a vacuum chamber for 24 h. Yield: ≈67%.

4.2.4 Synthesis of vanillin benzoxazine (Van-a)

A mixture of vanillin (0.033 mol, 5 g), aniline (0.033 mol, 3.07 g), and paraformaldehyde (0.066 mol, 1.97 g) were dissolved in 150 mL of chloroform and replaced in a flask equipped with a reflux condenser. The temperature was increased starting from room to reflux temperature over a period of 30 min then solution was refluxed 24h. After cooling to room temperature, unreacted compounds were extracted by 1 N NaOH solution (3 × 100 mL) and deionized water (2 × 100 mL). The chloroform layer was dried over anhydrous Na_2SO_4 and filtered, and the solvent was evaporated off. An oily light yellow compound was obtained. Yield: ≈71%.

4.2.5 Synthesis of allylbenzoxazine (Ba-ala)

A slightly modified procedure was used to synthesize Ba-ala monomer [3, 14]: First, allyamine (30.8 g, 0.54 mol) was dissolved in 1,4-dioxane (200 mL). This solution was cooled around 0 °C in an ice bath, and paraformaldehyde (32.5 g, 1.08 mol) was added to the cooled amine solution portion-wise during 10 min to prevent an exothermic amine− aldehyde reaction. After being certain that there was no gas evolution, bisphenol A (61.6 g, 0.27 mol) was added to the cold solution in one portion. The obtained solution was refluxed under an efficient cooler for 24 h. After the reaction content was cooled, 1,4-dioxane was removed from the flask under vacuum. The remaining sticky crude product was dissolved in diethyl ether (200 mL) and washed three times with 0.1 N sodium hydroxide solution and finally two times with deionized water for neutralization. The ether solution was dried with anhydrous Na_2SO_4 and filtered. After removal of diethyl ether, an oily viscous product was obtained. For further purification, this product was dissolved in 20 mL

of methanol and deionized water was added drop by drop until the solution became cloudy. At this point, the mixture was refrigerated at 4 °C overnight. The precipitated sticky yellowish mass was obtained by decantation of methanol and subsequent washing with deionized water. The product was dried at 60 °C under vacuum for 24 h (Yield: % 64).

4.2.6 Photoinduced post modification of polybutadienes by BPh-ptol or Van-a

BPh-ptol (100 mg, 0.50 mmol) or Van-a and PB (200 mg, 0.04 mmol) were placed in a pyrex tube with 4 mL CH_2Cl_2 and solution bubbled with dry nitrogen before sealing the tube. Irradiation was performed by using a Rayonet merry-go-round photo reactor with 16 lamps emitting light between 300−350 nm. After 48 h irradiation, (poly(butadiene-co-BPh-ptol) or poly(butadiene-co-Van-a) was precipitated in 10-fold excess hexane, decanted and washed with hexane 3 times and finally dried under vacuum at ambient temperature.

4.2.7 Film preparations and thermal curing

To obtain polybenzoxazine films, poly(butadiene-*co*-BPh-ptol) or poly(butadiene-*co*-Van-a) was mixed with B-ala monomer in $CHCl_3$ in 1:1 (w/w) ratio. $CHCl_3$ solutions were poured into a Teflon molds. The solvent was slowly evaporated at ambient temperature for 5 days. Then, the films were heated in an oven up to 200 °C gradually (1−2 °C/min) and kept at final temperature for 1 h. After cooling, cross-linked soft films were obtained.

4.3 Conclusion

The results presented in this paper demonstrate that benzoxazines equipped with aromatic carbonyl compounds can act as one component photoinitiators producing radicals by intermolecular hydrogen abstraction process. The two related compounds, BPh-ptol and Van-a, were synthesized through benzoxazine monomer synthesis methodology using 4-hydroxybenzophenone and vanillin, respectively as phenol source. Irradiation of PB in the presence of either compounds at $\lambda >$ 300−350 nm resulted in the incorporation of benzoxazine moieties into the polyolefin structure. These polymers can undergo thermal self-curing without using catalyst or curative.

Thermal investigations revealed that the curing temperature of the benzoxazine-modified PBs was increased slightly related to the dilution effect. Also, the thermal degradation behavior benzoxazine-modified PBs were also investigated and at 800 °C modified PBs gave higher char yield compared to pristine PB. The described photolytic process is valuable for expanding the usage of benzoxazines as high performance materials, and the method reported may be applied to other double bond containing polymers.

5. CONCLUSIONS

In this thesis, it was shown that benzoxazine chemistry is a flexible method to prepare high performance themosets with distinguished properties fulfilling various expectations of industrial applications. They provide possibilities not only to overcome some short-comings of traditional phenolic resins but also impart additional properties. In parallel to the extensive interest and publications in the benzoxazine based systems, this thesis demonstrates that potential new strategies are still possible to produce novel materials with unconventional properties. In the thesis, three distinct strategies were designed and applied in order to obtain functional high-performance materials.

First part of this thesis discusses overall background information to give more insight to basic principles of benzoxazine chemistry. Thus, synthetic techniques for benzoxazine monomers, polymerization mechanism of benzoxazines and functional benzoxazines are presented.

Second part of this thesis describes a simple and efficient approach for poly(propylene oxide)s bearing benzoxazine units (PPO-Benz) through supramolecular attractions. In the approach, PPO-Benz and carboxylic acid containing benzoxazine monomer were prepared through conventional polybenzoxazine synthesis methodology. These components mixed at suitable composition and heated to activate ring-opening reaction. The autonomous self-healing property of the film was investigated. The system is useful for further expanding the use of benzoxazines and may be extended to the other polymers.

In the third part, a new strategy to obtain sulfur rich polybenzoxazine copolymers was described. Elemental sulfur and allyl functional benzoxazines can thermally react to form polybenzoxazine copolymers. The methodology is easy and fast, which can be achieved in 30 min. and it can be called as inverse vulcanization of benzoxazines. The ring-opening reaction and inverse vulcanization take place simultaneously and/or sequentially producing copolymers in specific feed ratios. The approach giving opportunity to use it with different allyl functional benzoxazines. On the other hand, ring-opening temperature of benzoxazine is lower than bare

benzoxazine monomer due to the acidic medium. The simplicity of the process and low cost of the chemicals are the most important part of this strategy. Moreover, the approach presented here has some relevance to rubber technology where vulcanization is an important step and therefore may be adapted to create wider uses.

In the last part of the thesis, we designed and demonstrated a facile and generally applicable photochemical system usually employed for hydrogen abstraction UV curing of acrylate based formulations for benzoxazine chemistry. The concept involves the use of benzoxazine as both hydrogen donor and aromatic carbonyl photosensitizer. A side-chain benzoxazine functional polybutadienes was synthesized by photoinduced hydrogen abstraction process in one simple step. Irradiation of PB in the presence of related compounds at λ>300–350 nm resulted in the incorporation of benzoxazine moieties into the polyolefin structure without using any catalyst or curative. This photochemical system is important to obtain benzoxazine based high performance materials and this chemistry may be aplicable to other polymers which contains double bonds.

It is believed that the concepts presented here will open new pathways to further develop new chemistries for benzoxazine based high performance materials. Obviously, simplicity, cost and applications will be major concern for the new developments.

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